

Hydrocarbon Technologies, Inc.
P.O. Box 6047
New York & Puritan Avenues
Lawrenceville, New Jersey 08648
609/394-3102 Fax: 609/394-9602



Alfred G. Comolli
President

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**CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL
ELEVENTH QUARTERLY REPORT FOR THE PERIOD**

1 APRIL 1995 - 30 JUNE 1995

A.G. Comolli
E.S. Johanson
L.K. Lee
V.R. Pradhan
R.H. Stalzer

FINAL

WORK PERFORMED UNDER CONTRACT

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**HYDROCARBON TECHNOLOGIES, INC.
PO BOX 6047, NEW YORK & PURITAN AVENUES
LAWRENCEVILLE, NJ 08648**

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ABSTRACT

This quarterly report covers the activities of Catalytic Multi-Stage Liquefaction of Coal during the Period April 1 - June 30, 1995, at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. This DOE Contract Period was from December 8, 1992 to December 7, 1994 and has been extended to September 30, 1995.

The overall objective of this program is to produce liquid fuels from coal by direct liquefaction at a cost that is competitive with conventional fuels. Specifically, this continuous bench-scale program contains provisions to examine new ideas in areas such as: low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other hydrogen sources, more concentrated coal feeds and other highly responsive process improvements while assessing the design and economics of the bench-scale results.

This quarterly report covers work on Laboratory Scale Studies, Continuous Bench-Scale Operations, Technical Assessment and Project Management.

SUMMARY

This report describes the following: i) continuous bench-scale operations for Run CMSL-09 and ii) continuous bench-scale operations for Run CMSL-10.

Bench run CMSL-09 was a unique bench operation in that for the first time at HTI, a 41- day long continuous operation was carried out in an all-dispersed catalyst multi-stage reactor configuration. Similar to Run CMSL-08, an in-line hydrotreater was employed to lower the heteroatom content of the distillates. The overall operation was spread over nine run conditions. The effects of two dispersed catalysts, Molyvan-A, a cheap source of molybdenum, and HTI's iron catalyst, in their fresh as well as recycled forms, were studied for the multistage liquefaction of Wyoming Black Thunder Mine subbituminous coal. The last three conditions, spread over 12 operating days, also investigated coal/plastics coprocessing under steady-state recycle solvent-balanced conditions. During this time, effects of having 33 and 50 w% mixed plastics in the feed with coal were studied (mixed plastics were 40% HDPE, 33% PP, and 27% PS); one of the conditions also looked at the coprocessing of HDPE alone @ 33 w% with coal. Since dispersed catalysts were the only catalysts used in the reactors, a high feed throughput corresponding to a space velocity of 640 kg coal/hr/m³ reactor volume could be maintained.

CMSL-09 was a very successful bench run from a technical, as well as an operational, standpoint. A net positive solvent balance (excess production of 343°C+ oil over what is needed for recycle) was obtained for all the operating periods of this bench run. Over 41 days of continuous operation (12 days on coal/plastics coprocessing) were completed during CMSL-09 without any major interruptions. Samples of different process streams were also obtained for Consol, Inc. for property characterization/assessment. This bench run not only succeeded in providing insights into combined processing of coal with MSW plastics but also indicated the type of reaction severity, reactor configuration, and catalysts needed for achieving near-optimum process performance. So far as the effect of dispersed catalysts was concerned, it was once again observed that the molybdenum catalyst, freshly added as Molyvan-A precursor, is not as active in the recycled form as the freshly added form. The use of an in-line hydrotreater allows one the luxury of not having to use expensive supported metal extrudate catalysts in the liquefaction/coprocessing reactors. As long as the alternative dispersed slurry catalysts are cheap and effective for coal and resid conversions under the given process severity, the finishing of the light distillates to remove heteroatoms and to add more hydrogen can be achieved by an in-line hydrotreater.

Bench Run CMSL-10 (HTI Run 227-88) was designed as a follow-up study after the operation of Bench Run CMSL-09. During CMSL-09, for the first time at HTI, an all dispersed (slurry) catalyst reactor system was used for coal liquefaction and coal/waste plastics coprocessing. Interestingly, the performance of a multi-stage coal liquefaction unit, under a suitable reaction severity and with an in-line hydrotreater, was found to exceed the earlier process performance using ebullated bed reactors with supported catalysts. This result was very significant, as dispersed slurry catalysts, based on iron and molybdenum, employed during CMSL-09, are not only more economical to use than the supported catalysts, but they also have a tremendous potential to lower the overall operational costs for coal liquefaction by virtue of elimination of

the expensive ebullated bed reactors from the system. The effects of individual iron-based HTI propriety catalyst and molybdenum, added as Molyvan-A, were not fully understood during CMSL-09. One of the main objectives of run CMSL-10 was to further understanding of the effects of iron and molybdenum employed alone and added together. The mode of addition of HTI's iron catalyst and overall process severity (reactor temperatures and space velocity) were among the variables studied during CMSL-10.

After 18 periods of continuous operation, CMSL-10 was successfully completed with one brief shut-down. The results demonstrated that the combined system of Mo and FeOOH type catalysts improved process performance (iron alone was not very effective a catalyst). It was discovered that process performance remained the same even though iron catalyst (FeOOH/SO_4) was added as wet cake containing 70 W% water. This discovery has led to the further reduction on the catalyst cost by 30% due to the elimination of two time consuming/expensive processing steps in catalyst preparation. The space velocity and catalysts had an impact on the 524 °C+ conversion and distillate yield but did not seem to affect the total conversion. A slight change of the qualities of SOH and PFL was observed upon changing space velocity. This suggests that the current process can be operated at even higher throughput. The in-line hydrotreating was very effective for the removal of heteroatoms and for hydrogenation. The use of an in-line hydrotreator has resulted in the production of quality distillates which contain less than 50 ppm each of sulfur and nitrogen. The analysis of the qualities of samples from different process streams indicate that the current reactor configuration and combined system of Mo and Fe catalysts are effective in producing quality products from coal liquefaction. It is possible to establish a near-optimum process for coal liquefaction using a suitable combination of iron and molybdenum in low concentrations (5000 ppm for iron and 50-100 ppm for molybdenum) so that these dispersed catalysts can be employed on a disposable basis.

TASK 2 - LABORATORY SCALE STUDIES

No laboratory support work was conducted during this reporting period except for the analyses of the feeds and products from bench operations CMSL-09 and CMSL-10. These are discussed in the section on Bench-Scale Studies.

TASK 3 - BENCH-SCALE STUDIES

RUN CMSL-09 (227-87)

EVALUATION OF AN ALL DISPERSED SLURRY CATALYST MULTI-STAGE BACK-MIXED REACTOR SYSTEM FOR COAL LIQUEFACTION AND COAL/WASTE PLASTICS COPROCESSING

SUMMARY

Bench run CMSL-09 was a unique bench operation in that for the first time at HTI, a 41 day long continuous operation was carried out in an all-dispersed catalyst multi-stage reactor configuration. Similar to Run CMSL-08, an in-line hydrotreater was employed to lower the heteroatom content of the distillates. The overall operation was spread over nine run conditions. The effects of two dispersed catalysts, Molyvan-A, a cheap source of molybdenum, and HTI's iron catalyst, in their fresh as well as recycled forms, were studied for the multistage liquefaction of Wyoming Black Thunder Mine subbituminous coal. The last three conditions, spread over 12 operating days, also investigated coal/plastics coprocessing under steady-state recycle solvent-balanced conditions. During this time, effects of having 33 and 50 w% mixed plastics in the feed with coal were studied (mixed plastics were 40% HDPE, 33% PP, and 27% PS); one of the conditions also looked at the coprocessing of HDPE alone @ 33 w% with coal. Since dispersed catalysts were the only catalysts used in the reactors, a high feed throughput corresponding to a space velocity of 640 kg coal/hr/m³ reactor volume could be maintained.

The best performance for the 'coal-only' periods of CMSL-09 was obtained for Condition 1, Period 5. The resid conversion of about 92% and distillate yield of about 67% (both maf) were obtained at the process conditions shown and for 300 ppm of Mo, added as Molyvan-A, to the feed slurry. The overall process performance degraded in going from Condition 1 to 3 and then 4, i.e., in going from 300 ppm fresh Mo, to a combination of 150 ppm fresh and 150 ppm recycled Mo, and then to 300 ppm recycled Mo catalyst. The resid conversion during these transitions dropped by as much as 8%, while distillate yield decreased by 7% (both maf absolute bases). This trend in process performance confirms that molybdenum, in the recycled form, is not quite as active as fresh molybdenum, although this does not rule out that recycled molybdenum may possess some catalytic activity. Coal conversions, based upon quinoline solubility of the products, were uniform, at around 95-96 % maf throughout the 'coal-only' conditions, except for Condition 4 with all recycled Mo catalyst, when it decreased to 92.8% maf. Overall chemical hydrogen consumption varied between 6-7.5 % maf. The C₁-C₃ gas make varied between 10-11.5% maf coal.

The coal/plastics coprocessing operations during the last 12 days of CMSL-09 were successful in that Condition 7, Period 34, which coprocessed 33% mixed plastics with coal, gave as high as 75.4% distillate yield with over 92% (both maf bases) resid conversion. For Condition 8, Period 38, with 33% HDPE alone and 67% coal in the feed, the performance was poor (61% maf distillate yield and 79% maf resid conversion), confirming the poor reactivity of HDPE that was found during CMSL-08. Switching back to mixed plastics at 50% of total feed during Condition 9, Period 41, overall process performance jumped back to yield as high 75% distillates

and 88% resid conversion (maf). During Conditions 7 and 9 with mixed plastics much improved process performance over the earlier 'coal-only' conditions was obtained at a much reduced gas-make (7.5-8.5% maf) and lower chemical hydrogen consumption (3.5 to 5% maf). Thus, the coal/plastics coprocessing operations from both CMSL-09 and CMSL-08 resulted in improved overall process performance with better hydrogen utilization. This, we feel, will certainly improve the overall economics of coal conversion besides adding to it an environmental aspect.

The separator overhead oil products from CMSL-09 represent the net light distillate stream from the process. The overhead stream, which is essentially the liquids boiling between an initial boiling point of about 60°C and 370°C, represents a combination of hot separator (O-1) overhead and continuous atmospheric still (N-1 CAS) overhead streams which passed through the in-line hydrotreating unit, K-3. The product stream from K-3 is designated as the overall SOH (Separator OverHead) product. The other part of the distillate comes from the IBP to 524°C boiling fraction of the pressure filter liquid (PFL) or the vacuum still overheads (VSOH), which are used to constitute recycle solvent, depending upon what is used for solid separation of the CAS bottoms. The API gravities and H/C atomic ratios of the SOH oil from CMSL-09 have been high (35-43, and 1.73-1.82 respectively), especially for the coal/plastics coprocessing conditions. The quality of the distillates is also premium. The API gravities (an indication of paraffinic character) of the distillate increased significantly in going from the 'coal-only' conditions to 'coal/plastics' conditions (from about 32-37 to 40-44). The H/C ratios also improved during the transition. The light boiling naphtha (IBP-177°C) fraction increased significantly during the coprocessing conditions, except for the condition that coprocessed coal with HDPE alone, instead of mixed plastics. The sulfur and nitrogen contents of the distillate products were very low in general (10-100 ppm) and were even lower for the coal/plastics coprocessing conditions.

Overall process performance, using plastics in the feed with both coals independently, was much better with improved hydrogen utilization, a significant benefit one strives to derive from the plastics part of the feed in such coprocessing. Secondly, more so with a subbituminous coal (CMSL-09), it was found that plastics had a synergistic effect on coal conversion in terms of improving the C₄-524°C premium distillate yield. It was also learned that reactivity of HDPE, a hard-to-convert polymer, is improved under coal liquefaction conditions when other polymers such as polypropylene and polystyrene are present. This conclusion is based upon estimations of individual coal and plastics conversions to 524°C- material under reaction conditions. If it is assumed that 88-90% coal resid conversion is obtained along with complete conversions of both polypropylene and polystyrene, the conversion of HDPE in the presence of other polymers is about 12-35% higher than when HDPE is coprocessed alone with coal. Indeed, it is strongly believed that, because of all the positive effects of an all dispersed slurry catalyst reactor configuration and coprocessing waste plastics with coal, the economics of coal liquefaction will improve significantly. More importantly, such coprocessing technology would allow reuse of a very valuable hydrocarbon source (waste plastics) into the energy stream in an environmentally benign manner.

BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

Bench Run CMSL-09 was carried out using a dispersed catalyst-only two-stage, back-mixed reactor system. The two-stage conversion reactors were preceded by back-mixed pre-treatment reactor at lower temperature and half the capacity (volume) of each of the conversion reactors. The pretreatment reactor was intended for sulfidation of the dispersed catalyst additive. Bench run CMSL-09 was forty one days long, comprising nine operating conditions (3-5 days each). The objectives of this bench operation were:

- To determine the process performance for subbituminous coal liquefaction using a three-stage (including pretreater) dispersed catalyst-only back-mixed reactor system.
- To investigate the effect of molybdenum additive concentration on overall process performance.
- To determine the activity of fresh molybdenum catalyst vs. recycled moly catalyst.
- To study the effect of iron additive (in the presence of molybdenum), FeOOH/SO_4 , on process performance.
- To obtain a tie-point, for process performance comparisons, with reference to Exxon's latest coal liquefaction run using dispersed Fe/Mo catalysts, RCLU 1, Condition 4 (Yield Periods 422-424).
- To obtain performance data on plastics and coal coprocessing for variable feed compositions and at higher severity and in a dispersed catalyst-only system.

An in-line hydrotreater was used during this run. Both the hot separator (O-1) overheads and the atmospheric still overheads (ASOH) were sent through the hydrotreater. In order to obtain distillate samples that are not hydrotreated and to arrive at a mass-balance around hydrotreater, the HTU was bypassed during a few operating periods of the run.

The Run Plan (Table 1) included nine run conditions that were selected to meet the technical objectives specified above. By not using a supported extrudate catalyst in any of the coal liquefaction reactors, it became possible to compare the process performance of different run conditions on a one-to-one basis without being affected by 'catalyst batch-deactivation' phenomenon typical of bench CTSL operations. For the first five run conditions, 1 through 5, reactor temperatures and feed space velocities were maintained constant. These conditions studied the effects of varying the addition rate of molybdenum precursor and the relative activities of fresh vs. recycled moly catalyst. It is expected that molybdenum exists as MoS_x in the recycled solids (ash, char, and unconverted coal). Condition 5 studied the effect of adding FeOOH/SO_4 precursor/catalyst on overall process performance.

Condition 6 simulated the same operating conditions as those employed during Condition 4 (Yield Periods 422-424) of Exxon's RCLU Dispersed Slurry Catalyst Run 1. The objective was to obtain a tie-point for process performance comparison. Conditions 7 through 9 studied the combined processing of coal and plastics at different feed compositions and higher reactor temperatures than 'coal-only' Conditions 1 through 6.

Conditions 7 through 9 were designed to further our understanding of coal and waste plastics coprocessing using subbituminous coal and different feed compositions (w% plastics in feed), in an all dispersed catalyst reaction system. Mixed plastics (40% HDPE, 33% PP, and 27% PS) were used with coal at 33 and 50 w% feed composition during Conditions 7 and 9 respectively. The Condition 8 studied the effect of coprocessing 33 w% HDPE (a single plastic) in feed with coal, on the overall process performance.

SYSTEM CONFIGURATION:

CMSL-09 involved two equal volume backmixed reactors, a one half volume (1000 cc) pretreatment vessel (also back-mixed), and a fixed-bed hydrotreater. High pressure slurry samples were obtained both after the pretreatment vessel and after the first conversion reactor. The simplified schematic of this configuration is shown in Figure 1.

The reactors from existing units 227 and 238 were used in this run with the necessary re-piping and equipment modifications. A hot-slurry mix tank system was used throughout the run for slurry preparation. No supported catalyst was used in any of the conversion reactors, except in the hydrotreater (HTU). Hydrogen sulfide (H_2S), as a source of sulfur for the activation of dispersed iron and molybdenum additives, was continually added to the pretreater at 3 w% of dry coal.

COAL FEED AND WASTE PLASTICS

A subbituminous Black Thunder Mine Coal (HRI-6213), the same coal that was used in PDU 260-005 (POC-02 Run) operations, was used for the CMSL-09 (227-87) bench run. The waste plastics stream was simulated by using pure resins, such as HDPE, PS, and PP, in an extrudate form, co-mingled in the proportions representative of MSW plastics. The analyses of the coal and plastics are given in Table 2.

START-UP AND MAKE-UP OIL

Tank 4 material was L-814, a combination of hydrotreated petroleum-derived oil with small amounts of coal-derived liquid obtained during the operations of POC-02 PDU Run (Table 3).

CATALYST

Hydrotreater:

Pretreater (carried over to K-1 and K-2):

Criterion C-411 Trilobe (HRI-6135)
Molyvan-A, FeOOH/SO_4 , and 3 %
 H_2S relative to dry coal.

The dispersed acidic catalyst, FeOOH/SO_4 , was synthesized by aqueous precipitation in a solution containing sulfate anions. Molybdenum, or Molyvan-A, was obtained from R.T. Vanderbilt & Co.

RECYCLED-DISPERSED CATALYST

Oil-free pressure filter cake, extracted with toluene, was used as the source of the recycled-dispersed catalyst. The extracted filter cakes were dried to remove any residual solvent (toluene) and analyzed for molybdenum. Based on this analysis, the flowrate of the dried, extracted filter cake to the feed slurry was determined.

OPERATIONAL DETAILS

An average material balance of 99.25 W% was obtained (Figure 4) for the entire Bench Run CMSL-09. The operating summary of individual periods during CMSL-09 is shown in Table 4. Figures 2 and 3 show the operating conditions during CMSL-09 in terms of coal space velocity reactor temperatures, and feed pot (slurry mix tank) temperature. As shown in these figures, the pretreater and reactor temperatures are close to their desired values, and space velocities held at 640 kg/h/m^3 reactor throughout the run. It can also be seen in Figure 3 that due to the increased viscosity of feed, the slurry mix tank temperature had to be progressively increased to maintain the pumpability.

RECYCLE SOLVENT BALANCE

One of the primary objectives of CMSL-09 was to investigate the dispersed catalyst catalyzed direct coal liquefaction and coal/waste plastics coprocessing under steady-state or equilibrated process conditions. An important factor in such processing is the net recycle solvent/oil balance. This has to be positive to ensure that no external make-up oil is needed for slurry preparation, as the use of make-up oil would cloud the interpretation of the reaction data. It was feared that plastics, under typical coal liquefaction conditions, would result in substantial formations of light oils and a shortage of heavy recycle oil ($399^\circ\text{C}+$ material) would result. As shown in Figure 5, this was not the case. A net positive solvent balance was achieved almost throughout the entire run.

PROCESS PERFORMANCE

TOTAL FEED (COAL+PLASTICS) CONVERSION

Typical feed conversions (based on the solubility of pressure filter solids or vacuum still bottoms in quinoline) obtained during equilibrated periods of different conditions of CMSL-09 are shown in Figure 6. The feed conversion (W% maf feed) varied between 95-97% maf throughout the course of the run. Variations in the type and amount of dispersed catalyst additives did not seem to affect conversions significantly; presence of plastics in the feed also did not bring about any significant changes in overall feed conversion.

524°C+ RESIDUUM CONVERSION

Residuum conversion values varied between 79 to 92 W% (maf feed) and were more sensitive to the type and amount of the dispersed catalyst precursor added to the feed, as shown in Figure 6. Resid conversion levels were not significantly different for 200 and 300 ppm Mo added to the feed as Molyvan-A. Conversions dropped by about 6-7% maf when 300 ppm of Mo was used in the recycled-only form (by the addition of dried pressure filter cake). Resid conversion levels rose again as the iron catalyst was added to the feed with Molyvan-A and finally when the overall process severity was increased during the coal/plastics coprocessing operations. Similar to the observation made during CMSL-08, resid conversion during the coal+HDPE condition was the lowest (78.7 % maf), attesting to the conclusion that when HDPE is reacted individually with coal (without other plastics being present), it is difficult to convert to 524°C- material.

C₄-524°C DISTILLATE YIELDS AND SELECTIVITY

Distillate yields, shown in Figure 7, followed a similar trend in going from Condition 1 to 9 as did resid conversion. In general, the yields varied between about 60% to about 75 % maf during CMSL-09. For the coal-only conditions, the highest yield was obtained for Condition 1, 66.6% maf. During the coal/plastics coprocessing operations, a very high distillate yield of over 75% maf was obtained when 33% mixed plastics were processed with coal. High yields were maintained when the mixed plastics concentration in the feed was increased to 50%. Once again, as was the case during CMSL-08, distillate yields plummeted to about 61 % from 75 % when HDPE alone at 33% was coprocessed with coal.

So far as the selectivities of different boiling fractions of the net C₄-524°C distillate are concerned, the coal-only conditions resulted in 20-34% selectivity for the naphtha (C₄-177°C). This selectivity increased to about 40% during the coal/plastics coprocessing operations. Selectivity for middle distillates (177-343°C) varied only slightly for the different run conditions. Selectivity for heavy distillate (343-524°C) was the highest for Condition 8, which coprocessed HDPE alone with coal. Thus, Condition 8 resulted not only in poor total distillate yields but also in poor selectivity to light boiling fractions.

HYDROGEN CONSUMPTION

Hydrogen consumption (Figure 9) based on mf feed varied between 3.4 to 7.2 W%. During the 'coal-only' conditions, no specific trend or pattern was seen in hydrogen consumption with respect to variation in the type and the amount of dispersed catalyst. As expected, chemical hydrogen consumption decreased in going from the coal-only operating periods to the coal/mixed plastics coprocessing periods. This was due to lower light gas make during co-liquefaction operations and higher chemical hydrogen content of the combined feed. As the C₄-524°C distillate yield increased significantly in going from the 'coal-only' conditions to the coprocessing conditions, the hydrogen efficiency or utilization during coal/plastics operation is much better than 'coal-only' operation.

C₁-C₃ GAS YIELDS

As shown in Figure 9 and Table 4, normalized C₁-C₃ gas yields for CMSL-09 varied between 7.3 to 12.1 W% mf feed. Light gas yield was highest (12.1 W%) during the coal-only operation of Condition 3, and decreased significantly during coal/plastics co-liquefaction operations (Condition 7 through 9). The lowest gas yield was obtained during the last run condition which was with 50 % mixed plastics and coal. These findings indicate that mixed plastics do not form as much light hydrocarbon gas as the subbituminous coal feed.

524°C+ RESIDUUM YIELD

Residuum yield (Figure 9) was between about 4 % to about 16 % mf feed during CMSL-09. During the 'coal-only' conditions, residuum yield increased slowly as the amount of freshly added Mo catalyst was reduced from 300 ppm. Yields dropped when iron catalyst was added along with Molyvan-A. During coprocessing conditions, the highest resid yield was obtained for the Condition 8, which employed HDPE alone with coal. This observation also substantiates the refractory nature of HDPE towards conversion to light liquids and gases when coprocessed with coal, without any other plastics.

PRODUCT QUALITY

Different product fractions (First-Stage/Second-Stage Vent Gases, CAS Bottoms, SOH, ASOH, PFL, VSOH and PFS/VSB) from Work-up Periods 5, 9, 15, 19, 24, 29, 34, 38, and 41 were analyzed in detail. These analyses for different product fractions are listed in Tables 6 through 11.

Separator Overhead Product (SOH) and Atmospheric Still Overhead Product (ASOH)

SOH oil stream represented the net light distillate (IBP-343°C) from CMSL-09. While the hydrotreater was on-line during the run, the only major distillate stream out of the unit was SOH, as O-1 hot separator overheads, ASOH, and unit knockouts were being fed directly to the

hydrotreater. The properties of SOH oil for the work-up periods are shown in Table 6. The SOH oils had a typical boiling range of 54-399°C. The API gravities were high (> 35), and H/C atomic ratios were also high (1.73-1.82), especially during coal-plastics coprocessing. The yield of IBP-177°C, the lightest fraction of the SOH-oil, was also higher during co-liquefaction than for coal-only Condition 1. Heteroatom (nitrogen and sulfur) levels were low throughout the run, indicating very successful operation of the in-line hydrotreater. Typically, sulfur levels below 15 ppm and nitrogen levels below 50 ppm were obtained for the SOH oil. (It is believed that during Periods 24 and 29, the quality of the SOH oil stream was affected by a residual effect of bypassing of the HTU during Periods 23 and 28.)

The ASOH stream is obtained from the unit as a sample stream only. As seen from Table 7, this unhydrotreated oil stream has a low API gravity (4-14) except during coprocessing. The quality is also poor, i.e., high sulfur (200-375 ppm) and nitrogen (150-741 ppm) contents and low H/C atomic ratios (1.17-1.53). This stream, combined with the hot separator overheads (O-1) and unit knockouts, goes to the in-line hydrotreater for finishing.

The separator overhead oil from CMSL-09 represent the net light distillate stream from the process. The overhead stream, which is essentially the liquids boiling between about 60°C and 370°C, represents a combination of the hot separator (O-1) overhead and the continuous atmospheric still (N-1 CAS) overhead streams which passes through in-line hydrotreating unit, K-3. The product stream from K-3 is designated as overall SOH (Separator OverHead) product. The other part of the distillate comes from the IBP to 524°C boiling fraction of the pressure filter liquid (PFL) or the vacuum still overheads (VSOH), which are used to constitute recycle solvent, depending upon what process is used for solid separation of the CAS bottoms. The API gravities and H/C atomic ratios of the SOH oil from CMSL-09 are high (35-43, and 1.73-1.82 respectively), especially for the coal/plastics coprocessing conditions. The quality of the distillates is also premium. The API gravity (an indication of paraffinic character) of the distillate increased significantly (from about 32-37 to 40-44) in going from 'coal-only' conditions to 'coal/plastics' conditions. The H/C ratios also improved during the transition. The light boiling naphtha (IBP-177°C) fraction increased significantly during the coprocessing conditions, except for the condition that coprocessed coal with HDPE alone. The sulfur and nitrogen contents of the distillate products are very low in general (10-100 ppm), and even lower for the coal/plastics coprocessing conditions.

SIGNIFICANT FINDINGS FROM CMSL-09

(I) Effect of Type and Amount of Dispersed Catalyst

One of the objectives of CMSL-09 was to investigate the effect of dispersed molybdenum and iron catalysts on process performance. Four molybdenum concentrations were studied: 300 ppm fresh, 200 ppm fresh, 150 ppm fresh plus 150 ppm recycle, and 300 ppm recycle-only. It was observed, under equivalent process severity conditions, that the molybdenum catalyst in freshly added precursor form was more active for coal residuum conversion than recycled molybdenum catalyst. Addition of 1 w% iron catalyst (FeOOH/SO_4) during Condition 6 was found to improve

the overall process performance slightly over Condition 5 (which used 150 ppm fresh Mo and 150 ppm recycled Mo). The source of the recycled catalyst in most cases was the Continuous Atmospheric Bottoms (CAS Bottoms) stream; during Condition 4, which was with 300 ppm recycled-only Mo catalyst, a dried and toluene-extracted pressure filter cake, derived from the earlier periods of the run, had to be used. The observation made during this run on the relative activities of fresh vs. recycled Mo catalysts is consistent with what was seen with sulfated iron oxide catalyst during an earlier bench run, CMSL-06. As part of the follow-up of this finding, a few microautoclave batch tests are being planned to study the catalytic behavior of both fresh Molyvan-A and the dried pressure filter cakes from CMSL-09.

(II) Effects of Feed Composition:

The first six conditions during CMSL-09 were 'coal-only' feed conditions. It was during the last three conditions that coal/plastics coprocessing was carried out. The coal/plastics coprocessing operations during the last 12 days of CMSL-09 were successful in that during Condition 7, Period 34, which coprocessed 33% mixed plastics with coal, as high as 75.4% distillate yield was obtained with over 92% (both maf bases) resid conversion. Next, for Condition 8, Period 38, with 33% HDPE alone and 67% coal in the feed, the performance was poor (61% maf distillate yield and 79% maf resid conversion), confirming the poor reactivity of HDPE that was found during CMSL-08. Switching back to mixed plastics, at 50% of total feed during Condition 9, Period 41, overall process performance jumped back to as high as 75% distillates and 88% resid conversion (maf). During Conditions 7 and 9, with mixed plastics, much improved process performance over the earlier 'coal-only' conditions was obtained at a much reduced gas-make (7.5-8.5% maf) and lower chemical hydrogen consumption (3.5 to 5% maf).

(III) Hydrotreater Performance:

The in-line hydrotreater has performed well during CMSL-09, as exemplified by the low heteroatom contents of the distillate products and their high H/C ratios. The absolute N and S contents are not as low as those obtained during CMSL-08, because for the first time a high space velocity of 640 kg/h/m³ reactor was used, coupled with the fact that it was an all dispersed-catalyst based reactor system. Thus, there was no supported catalyst in the second coal liquefaction stage for products upgrading as in the more conventional CTSL type configuration. Table 5 summarizes the poor quality of the distillate product streams when the HTU was by-passed, with nitrogen and sulfur contents as high as 350 ppm. Upon hydrotreatment, as indicated by the shaded portions of Table 5, the SOH distillates had less than about 50 ppm nitrogen and sulfur.

(IV) Reactivity of High Density Polyethylene (HDPE):

CMSL-09 was an extension of our efforts during CMSL-08, to define a near-optimum set of catalysts/operating conditions to improve the total conversion of mixed plastics into useful liquid products. One of the main findings during CMSL-08 was the refractory nature of HDPE towards cracking/depolymerization, especially when fed by itself (without other plastics) with coal. Similar effects were observed during CMSL-09, with a different type of coal feed and under a different set of operating conditions and catalysts. Estimations of the conversion of HDPE to 524°C-material are based on assuming 88% conversion of the coal residuum and 100% conversion of other plastics (PP and PS) into 524°C- materials (and correlating them with the actual conversions of the combined feeds to 524°C- materials). These are shown in Figure 11. For Condition 7 which employed mixed plastics with coal, over 90% conversion of HDPE is estimated, while for the Condition 8, when HDPE alone was coprocessed with coal, HDPE conversion is estimated to be only 56%. In Condition 9, with mixed plastics and coal, estimated HDPE conversion increased by more than 10%. This behavior seems to indicate that the presence of other plastics may be instrumental in improving reactivity of HDPE under our coprocessing conditions.

(V) Comparison with Exxon's Dispersed Catalyst Data:

Condition 6 of Bench Run CMSL-09 was designed to obtain a tie-point for comparison between HTI's data and Exxon's data. Two dispersed catalysts were employed during these conditions: iron and molybdenum. At HTI, Molyvan-A was used as a source of molybdenum at 100 ppm relative to coal, while sulfated iron oxide, prepared at HTI, was used as a source of iron at 1 w% relative to coal. Process performance comparisons are summarized in Table 13. Operating conditions were very similar for HTI's Condition 6 and Exxon's Conditions 3 and 4. Exxon had employed both Molyvan-A and Molyvan-L as Mo precursors, while for iron, Exxon employed Baily's -325 mesh iron oxide during Condition 3 of their run and Bayferrox fine-sized iron oxide during Condition 4. From Table 13, it can be seen that under similar conditions and catalyst loadings, HTI's Condition 6 resulted in better overall process performance. Distillate yields are about 2.5% higher and so are 524°C+ residuum conversions. Light gas yields are slightly lower for HTI's Condition 6, while hydrogen consumption is slightly higher, meaning the increased hydrogen consumption was utilized for the production of useful liquid products. Since all the operating conditions and Mo precursors were the same for HTI's Condition 6 and Exxon's Conditions 3 & 4, it can be said that the better overall process performance at HTI is attributable to the use of a more active iron precursor/catalyst i.e., HTI's FeOOH/SO₄ catalyst.

The positive influence of the addition of 1 w% FeOOH/SO₄ catalyst was also seen on the recycle system during CMSL-09. Towards the end of Period 9 (Condition 2), the nature of the resid material in the CAS bottoms was such that pressure filtrations became very time-consuming and finally not doable. At this point solids separation was changed to vacuum still operation. This continued well until the point in the run when an addition of iron catalyst was begun. Soon after iron catalyst was introduced with the feed at 1 w% level, the nature of the resid in the CAS bottoms changed to make pressure filtration operable with short turn-around times.

INTERSTAGE SAMPLES

Interstage samples are samples of the slurry exiting the first stage coal liquefaction reactor that are withdrawn from the ebullating line on the reactor (analyses shown in Tables 10 and 11). These samples shed light on the performance of the first stage reactor in terms of coal and resid conversions. Interstage samples of product slurry from the first stage reactor were collected during all the work-up periods of CMSL-09. Analyses of the pressure filter solids from these samples indicates that about 93-94% coal conversion (based on quinoline solubility) is obtained after the first stage coal liquefaction reactor. The properties of the interstage (first stage) PFL are very consistent with the data-trends discussed earlier in this report.

EXTERNAL SAMPLES

As mentioned earlier, a number of samples of different process streams from CMSL-09 were obtained (for further detailed characterization and products assessment) for Consol, Inc. and also for members of the Consortium of Fossil Fuel Liquefaction Science. These samples, their amounts, and the operating periods when they were withdrawn are shown in Table 12.

CONCLUSIONS

CMSL-09 was a very successful bench run from both the technical and operational standpoints. Over 41 days of continuous operation was completed without any major issues/interruptions, and the main technical objectives of the run were achieved. The effects of type and amount of molybdenum based dispersed catalysts were studied, as well as two plastics/coal ratios, effects of HDPE alone, and high space velocity. Samples of different process streams were obtained for property characterization/assessment. The following conclusions can be drawn based on results from this run:

- The CTSL type reactor configuration, with an all dispersed catalyst system, results in good overall process performance, even at high feed space velocities (coal conversions over 95%, resid conversions over 90%, and distillate yields of over 66%) with a sub-bituminous coal feed.
- Process performance degraded only slightly with a decrease in fresh Mo addition. Process performance was better with fresh molybdenum precursor than with recycled catalyst. HTI's sulfated iron catalyst improved overall performance when used at 1 w% loading relative to feed.
- Both 33% and 50% mixed plastics with coal resulted in significant improvements in distillate liquids (as high as 10-12% maf) over 'coal-only' conditions.
- HDPE alone, with coal, was found much harder to convert to 524°C- material than when other plastics were present co-mingled form.

- In-line hydrotreating was very effective for producing premium distillates with less than 50ppm sulfur and nitrogen.

Based upon the interesting results obtained during the last three conditions of CMSL-09 on coal/plastics coprocessing, more studies are certainly warranted for the optimization of dispersed catalyst type and level, convertibility of HDPE to light liquids, and impact of such coprocessing on the product quality and end-use applications. It will be very interesting to follow findings from this bench run with another bench operation with the 'real life' MSW plastics. Also, the efficacy of the dispersed catalyst reactor configuration should be investigated for low quality petroleum resids/waste plastics/coal coprocessing operations.

TABLE 1

CMSL-09 Run Plan

Condition	1	2	3	4	5	6	7	8	9
Periods	1-5	6-9	10-14	15-19	20-24	25-29	30-34	35-38	39-41
Feeds, W%									
Coal	100	100	100	100	100	100	67	67	50
HDPE	0	0	0	0	0	0	13	33	20
Polypropylene	0	0	0	0	0	0	11	0	16.5
Polystyrene	0	0	0	0	0	0	9	0	13.5
Temp. deg C									
Pretreater	300	300	300	300	300	300	300	300	300
K-1	443	443	443	443	443	440	449	449	449
K-2	449	449	449	449	449	449	460	460	460
HTU	379	379	379	379	379	379	379	379	379
Space Velocity (Kg feed/hr/m3)	640	640	640	640	640	640	640	640	640
Slurry Cat. Conc. parts per million									
Mo: Molyvan-A									
-Fresh	300	200	150	0	150	100	300	300	300
-Recycled	0	0	150	300	150	100	300	0	0
FeOOH/SO4	0	0	0	0	0	10000	10000	10000	10000
Solid Separation**	PF	PF	VS	VS	VS	VS	VS	PF	PF

*Tie-Point Condition for Comparison with Exxon's latest Dispersed Catalyst Run.

** PF - Pressure Filter; VS - Vacuum Still

TABLE 2

' Analysis of coal and plastic* feedstocks for CMSL-09.

Material	BTM Coal	HDPE	Polystyrene	Polypropylene
Moisture Content	10.1			
Elemental, w% dry				
Carbon	70.12	85.71	92.31	85.71
Hydrogen	5.11	14.29	7.69	14.29
Sulfur	0.35	0	0	0
Nitrogen	0.99	0	0	0
Oxygen (by diff.)	17.24	0	0	0
Ash, % dry	6.19	0	0	0
H/C Atomic Ratio	0.88	2	1	2

*All three plastics were initially completely insoluble in either quinoline or cyclohexane.

TABLE 3**Analysis of start-up/make-up oil for CMSL-09**

HTI No.	L-814
API Gravity	0.4
Elemental Analysis, W %	
Carbon	88.96
Hydrogen	8.25
Sulfur	2.22
Nitrogen	0.19
ASTM D-1160 Distillation, deg C	
IBP	309
5 V %	351
10 V %	374
20 V %	394
30 V %	409
40 V %	426
50 V %	437
60 V %	449
70 V %	467
80 V %	507
84 V %	524
WEIGHT PERCENTS	
IBP-343 Deg C	5
343-454 Deg C	53.99
454-524 Deg C	22.18
524 Deg C +	18.36
LOSS	0.47
% Aromatic Carbon	80.03
% Cyclic Hydrogen	44.36

TABLE 4

CMSL-09: PROCESS PERFORMANCE SUMMARY

Unit	227	227	227	227	227	227	227	227	227
Run	87	87	87	87	87	87	87	87	87
Condition	1	2	3	4	5	6	7	8	9
Period Number	5	9*	15	19	24	29	34	38	41
Hours of Run (end of Period)	120	216	360	456	576	696	816	912	984
W% Plastics in Feed	0	0	0	0	0	0	33	33	50
Disp. Cat. ppm: Fresh Mo	300	200	150	0	150	100	300	300	300
Rec. Mo	0	0	150	300	150	100	300	0	0
Fresh Iron	0	0	0	0	0	10000	10000	10000	10000
Stage I Feed Space Velocity									
kg coal/hr/m3 reactor vol.	680	666	659	664	678	666	669	709	669
Temperatures, C									
Pretreater	304	302	302	303	302	305	318	316	315
K-1	444	444	445	443	444	440	448	448	449
K-2	449	450	450	449	449	449	459	461	462
Total Material Recovery % (Gross)	98.7	102.7	98.5	99.6	100.9	103.8	99.2	99.1	102.1
ESTIMATED NORMALIZED YIELDS:									
W% DRY FEED									
C1-C3 in Gases	10.96	10.55	12.08	9.30	10.74	9.23	8.18	7.45	7.31
C4-C7 in Gases	4.30	4.25	4.96	4.10	4.71	4.66	4.51	4.65	5.44
IBP-177 deg C	17.24	13.45	14.26	13.10	14.44	7.37	21.43	8.52	23.64
177-260 deg C	12.15	13.07	14.62	11.79	14.20	15.64	14.87	10.32	11.54
260-343 deg C	17.19	14.05	15.71	14.41	15.75	14.92	16.31	12.18	13.88
343-454 deg C	10.22	12.48	6.77	7.45	6.26	12.44	11.41	18.31	13.26
454-524 deg C	1.69	2.37	2.26	5.66	3.46	4.01	3.92	4.6	4.31
524 deg C+	3.70	5.18	5.78	10.21	7.88	7.35	2.16	16.14	8.61
Unconverted Feed	3.93	3.93	4.55	4.44	4.77	4.34	5.41	4.31	2.92
Water	15.23	14.77	13.22	15.58	12.76	14.96	10.26	10.5	7.15
COx	3.78	5.37	5.59	3.10	4.81	4.38	1.67	2.82	2.07
NH3	1.02	0.97	0.97	0.88	0.88	0.86	0.56	0.51	0.38
H2S	0.03	-0.03	0.16	0.08	-0.17	-0.15	-0.05	-0.1	-0.04
Hydrogen Consumption	7.20	6.17	6.69	5.87	6.26	5.75	4.56	4.14	3.43
PROCESS PERFORMANCE									
Feed Conversion, W% maf Feed	95.8	95.8	95.2	95.2	95.1	96.1	95.3	95.5	97.0
524 C+ Conversion, W% maf Feed	91.9	90.3	89.0	84.4	86.6	87.6	92.1	78.7	88.1
C4-524 C Distillates, W% maf Feed	66.6	63.3	62.2	60.0	62.4	62.6	75.4	61.0	74.3

*Data from Period 8 has been used to evaluate the Work-up Period 9.

TABLE 5

Hydrotreater Performance during CMSL-09

[All numbers in parts per million]

HTU Off-line			HTU On-line*	
<u>Period 23</u>			<u>Period 19</u>	
	<i>Nitrogen</i>	<i>Sulfur</i>	<i>Nitrogen</i>	<i>Sulfur</i>
ASOH	331.1	362	303.1	281
SOH	332.5	160.4	60.6	9.4
<u>Period 8</u>			<u>Period 10</u>	
	<i>Nitrogen</i>	<i>Sulfur</i>	<i>Nitrogen</i>	<i>Sulfur</i>
ASOH	172	298.1	150.2	338.6
SOH	230.1	265.3	25.6	17.9

*The shaded numbers are for Hydrotreated Distillate Products.

CMSL-09: SEPARATOR OVERHEAD (SOH) INSPECTION

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TABLE 7

CMSL-09: ATMOSPHERIC OVERHEAD (ASOH) INSPECTION

Unit	227	227	227	227	227	227	227	227	227
Run	87	87	87	87	87	87	87	87	87
Condition	1	2	3	4	5	6	7	8	
Period #	5	9	15	19	24	29	34	38	
Gravity, API	12.9	10.6	14.2	14	13.6	3.3	27	24.4	
IBP (deg C)	77.8	167.8	88.9	78.3	77.2	75.6	71.1	80.6	
FBP (deg C)	393.9	395.6	392.2	389.4	391.1	390.0	392.2	398.3	
ASTM D-86 Distillation, Composition									
W% IBP-177 deg C	7.86	0	6.2	5.3	5.6	4.1	30.3	16.6	
W% 177-260	22.35	14.1	25.8	23.3	22.4	16.1	25.1	32.5	
W% 260-343	35	51.1	43.7	44.9	44.6	29.05	29.7	25.4	
W% 343+	34.69	34.4	24.3	26	26.9	50.47	14.6	25.2	
W% Loss	0.1	0.4	0	0.5	0.5	0.28	0.3	0.3	
Elemental Analysis									
Carbon, W%	85.69	86.18	85.92	85.88	86.05	79.92	85.82	84.54	
Hydrogen, W%	9.63	9.19	9.6	9.53	9.53	7.77	10.51	10.79	
Sulfur (Antek), ppm	375.7	338.6	298.1	281	362	290	205	352	
Nitrogen (Antek), ppm	263.6	150.2	172	303.1	331.1	372	692.6	741	
H/C Ratio	1.35	1.28	1.34	1.33	1.33	1.17	1.47	1.53	

CMSL-09: PROPERTIES OF THE PRESSURE FILTER LIQUID (2nd Stage)*

*For Periods 9-34, since vacuum still was used in place of pressure filtration for solids separation, the analysis of VSOH is listed.

TABLE 9

CMSL-09: INSPECTION OF THE PRESSURE FILTER SOLID (2nd Stage)*

Unit Run Condition Period #	227 87 1 5	227 87 2 9	227 87 3 15	227 87 4 19	227 87 5 24	227 87 6 29	227 87 7 34	227 87 8 38	227 87 9 41
Elemental Analysis									
Carbon, W%	60.27	72.88	59.05	59.65	58.35	58.5	63.65	54.99	50.93
Hydrogen, W%	3.96	4.31	3	3.34	3.13	3.14	4.97	3.32	3
Sulfur, W%	1.53	0.784	1.07	1.04	1.08	2.21	1.54	3.5	1.53
Nitrogen, W%	0.58	1.01	0.81	0.85	0.77	0.79	0.64	0.7	0.75
H/C Ratio	0.79	0.71	0.61	0.67	0.64	0.64	0.94	0.72	0.71
Composition, W%									
Ash (Quinoline Filtration)	31.18	16.53	30.58	28.33	30.05	32.58	26.17	36.75	42.64
ASTM Ash	29.48	16.99	31.06	30.11	30.87	33.44	26.97	37.88	43.56
Sulfur in Ash	3.4	3.8	2.32	2.85	3.06	5.65	4.34	7.89	3.4
QI Including Ash	49.12	28.73	51.24	47.1	51.55	49.75	54.78	65.24	69.39
Metals Analysis, w%									
Molybdenum	0.443	0.508	0.365	0.224	0.334	0.256	0.56	0.654	1.55
Iron	3.99	3.486	3.32	3.35	3.29	7.47	6.13	8.1	13.39

* Periods 9-34, since vacuum still was used for solids separation, the analyses of VSB are listed.

TABLE 10

CMSL-09: PROPERTIES OF THE PRESSURE FILTER LIQUID (1st Stage)

Unit	227	227	227	227	227	227	227
Run	87	87	87	87	87	87	87
Condition	1	2	3	4	5	6	7
Period #	5	9	15	19	24	29	34
Gravity, API	-6.2	-3.1	-3	-4.6	-3.7	-0.6	4
IBP (deg C)	223.333	217.222	228.333	236.667	222.778	225	252.222
ASTM D-1160 Distillation, Composition							
W% IBP-343 deg C	10.98	15.61	14.17	12.47	16.35	14.61	11.3
W% 343-454	36.94	42.47	37.33	39.55	37.4	42.74	39.85
W% 454-524	14.35	13.98	13.99	12.83	13.28	15.08	11.49
W% 524+	37.02	27.22	33.79	34.71	32.34	26.83	36.97
W% Loss	0.71	0.72	0.72	0.44	0.63	0.74	0.39
Elemental Analysis							
Carbon, W%	88.3	87.54	87.57	87.87	87.91	87.64	88.38
Hydrogen, W%	7.05	7.53	7.62	7.48	7.42	7.79	9.22
Sulfur, W%	0.82	0.543	0.412	0.274	0.299	0.496	0.201
Nitrogen, W%	0.79	0.96	0.99	1.06	1.02	0.89	0.75
H/C Ratio	0.96	1.03	1.04	1.02	1.01	1.07	1.25
CCR, W% PFL	59.85	53.46	49.21	51.76	54.88	53.15	33.59
Cyclohexane Insolubles, W%		66.66	56.27	63.94	64.24	55.27	59.48
Toluene Insolubles, W%		21.55	17.27	16.65	18.62	16.07	24.75

TABLE 11

CMSL-09: INSPECTION OF THE PRESSURE FILTER SOLID (1st Stage)

Unit	227	227	227	227	227	227	227
Run	87	87	87	87	87	87	87
Condition	1	2	3	4	5	6	7
Period #	5	9	15	19	24	29	34
Elemental Analysis							
Carbon, W%	60.82	55.46	56.43	56.01	55.78	55.6	53.72
Hydrogen, W%	3.8	3.43	3.64	3.5	3.59	3.7	3.91
Sulfur, W%	1.57	1.29	1.53	1.38	1.2	2.78	2.69
Nitrogen, W%	0.75	0.7	0.66	0.67	0.68	0.66	0.6
H/C Ratio	0.75	0.74	0.77	0.75	0.77	0.80	0.87
Composition, W%							
Ash (Quinoline Filtration)	26.11	30.99	31.03	32.49	32.14	35.71	37.07
ASTM Ash	26.82	30.92	31.33	33	32.5	37.26	37.75
Sulfur in Ash	3.61	3.41	3.76	3.52	3.16	6.33	5.61
QI including Ash	51.66	59.38	53.99	54.49	54.9	59.62	65.71

TABLE 12

Hydrocarbon Technologies, Inc.

SHIPPING REQUEST FORM

<u>Requested By :</u> Vivek Pradhan	<u>Need Date</u> 05/25/95	<u>WO Number</u> 846-339	<u>Date Sub.</u> 05/19/95																																	
<u>Sample Description & Amounts:</u> <div style="float: right;"><u>File with:</u> 227-87</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 40%;">1. FEED SLURRY</td> <td style="width: 15%;">250 GM</td> <td style="width: 45%;">PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>2. CAS BOTTOMS</td> <td>350 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>3. SOH OIL</td> <td>250 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>4. ASOH MATERIAL</td> <td>250 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38</td> </tr> <tr> <td>5. PRESSURE FILTER LIQUID (OR VACUUM STILL OVERHEADS)</td> <td>350 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>6. PRESSURE FILTER SOLID (OR VACUUM STILL BOTTOMS)</td> <td>350 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>7. INTERSTAGE (K-2) SLURRY</td> <td>350 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>8. FEED SLURRY</td> <td>250 GM</td> <td>PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41</td> </tr> <tr> <td>9. HDPE</td> <td>300 GM</td> <td></td> </tr> <tr> <td>10. POLYPROPYLENE</td> <td>300 GM</td> <td></td> </tr> <tr> <td>11. POLYSTYRENE</td> <td>300 GM</td> <td></td> </tr> </table>				1. FEED SLURRY	250 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	2. CAS BOTTOMS	350 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	3. SOH OIL	250 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	4. ASOH MATERIAL	250 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38	5. PRESSURE FILTER LIQUID (OR VACUUM STILL OVERHEADS)	350 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	6. PRESSURE FILTER SOLID (OR VACUUM STILL BOTTOMS)	350 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	7. INTERSTAGE (K-2) SLURRY	350 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	8. FEED SLURRY	250 GM	PERIODS 5, 9, 15, 19, 24, 29, 34, 38, 41	9. HDPE	300 GM		10. POLYPROPYLENE	300 GM		11. POLYSTYRENE	300 GM	
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<u>Special Instructions:</u> [PLEASE ENCLOSE THE MSDS INFORMATION WITH THE SHIPMENT]																																				
<u>WHERE DO SAMPLES GO?</u> Attention: DR. GARY ROBBINS CONSOL, INC. R & D 400 BROWNSVILLE ROAD LIBRARY, PA 15129.																																				
AUTHORIZED: (THEO L. K. LEE)																																				

TABLE 13**Comparison Between CMSL-09 Condition 6 and Exxon's Data**

Run	HTI*	Exxon	Exxon
Condition	6	3	4
Residence Time, min	40	41	41
Temperatures, deg C			
Pretreater	300	300	300
Reactor K-1	440	441	439
Reactor K-2	449	450	450
Hydrotreater	379	N/A	N/A
Dispersed Catalysts			
Molybdenum	Molyvan-A	Molyvan- A	Molyvan-L
ppm	100 ppm	100 ppm	100 ppm
Iron	FeOOH/SO4	Baily	Bayferrox
w%	1 %	1 %	1 %
Yields (MAF)			
C1-C3	9.8	10.8	10.2
C4-538 C	62.6	59	60
C4-177 C	12.8	14.8	15
177-343 C	32.4	29.6	31.3
343-538 C	17.4	14.6	13.7
Coal Conversion, %maf	96.1	n/a	n/a
538 C+ Resid Conv., % maf	87.6	86.9	85.6
Hydrogen Consumption, %maf	6.1	5.8	5.4

* HTI's data represents the C4-524 C distillate fraction and 524 C+ Resid Conversion instead of C4-538 C yield and 538 C+ Resid conversions in Exxon's data.

FIGURE 1

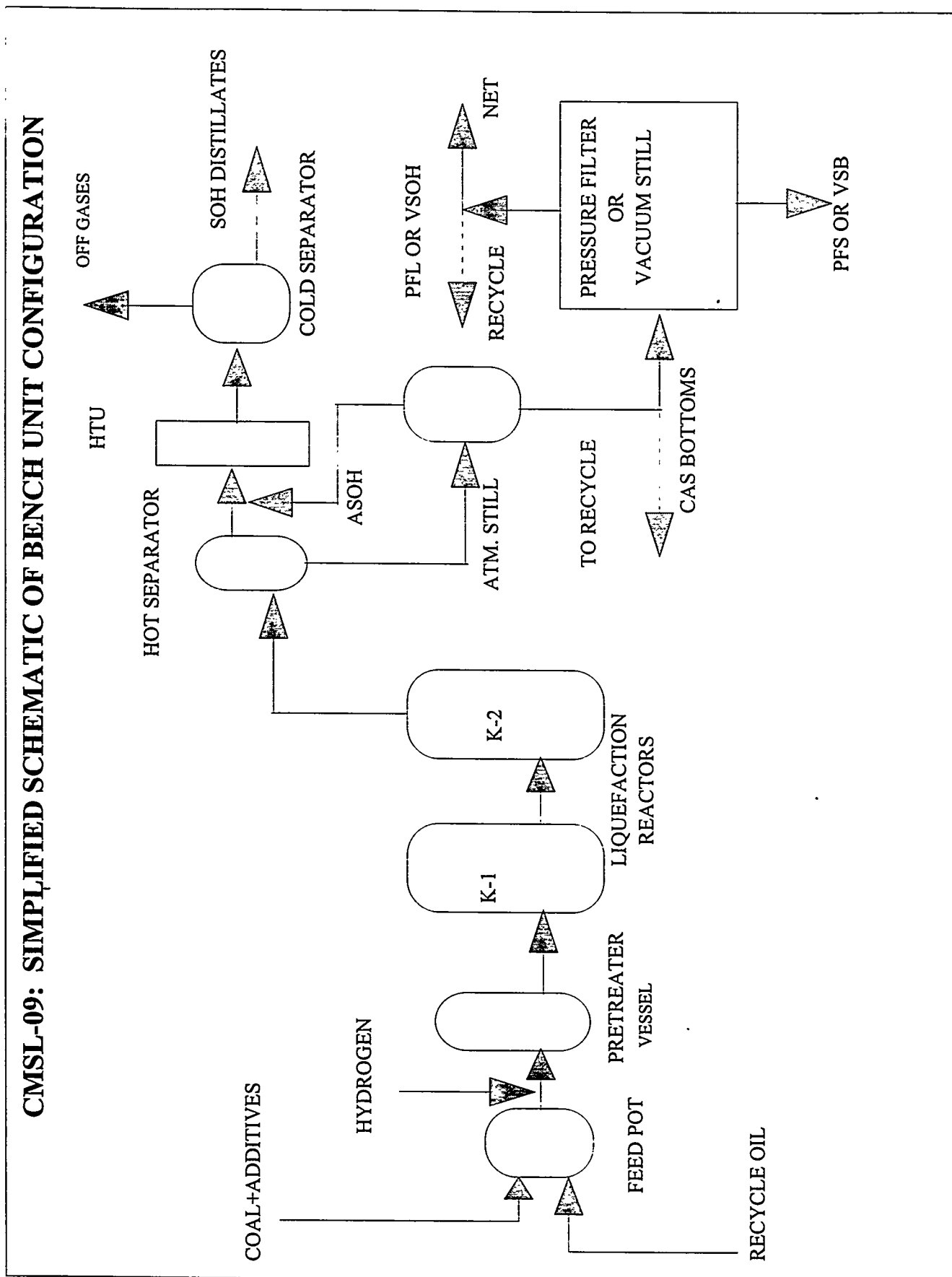


FIGURE 2

CMSL-09: Reactor Temperatures

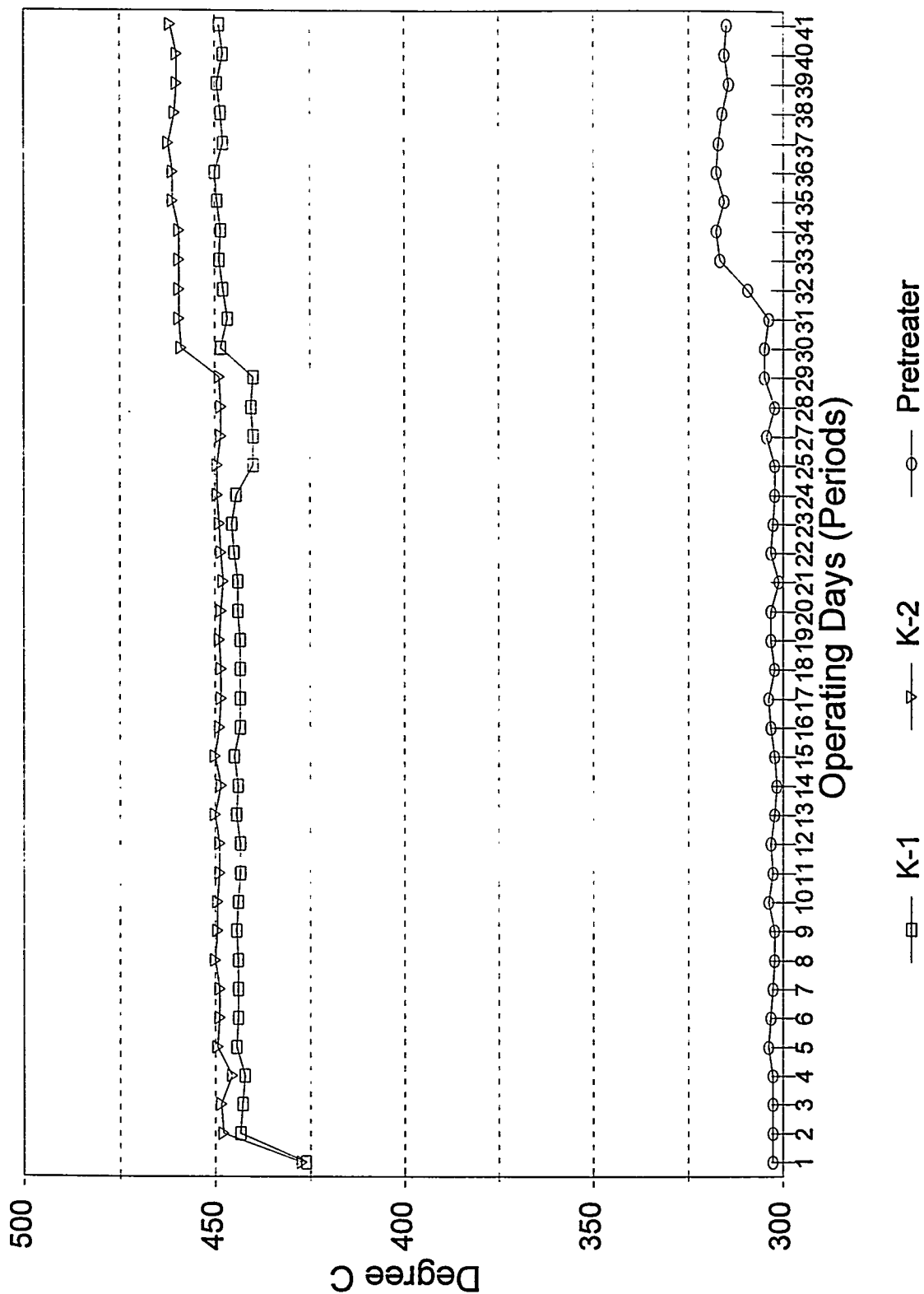


FIGURE 3

CMSL-09: Operating Conditions

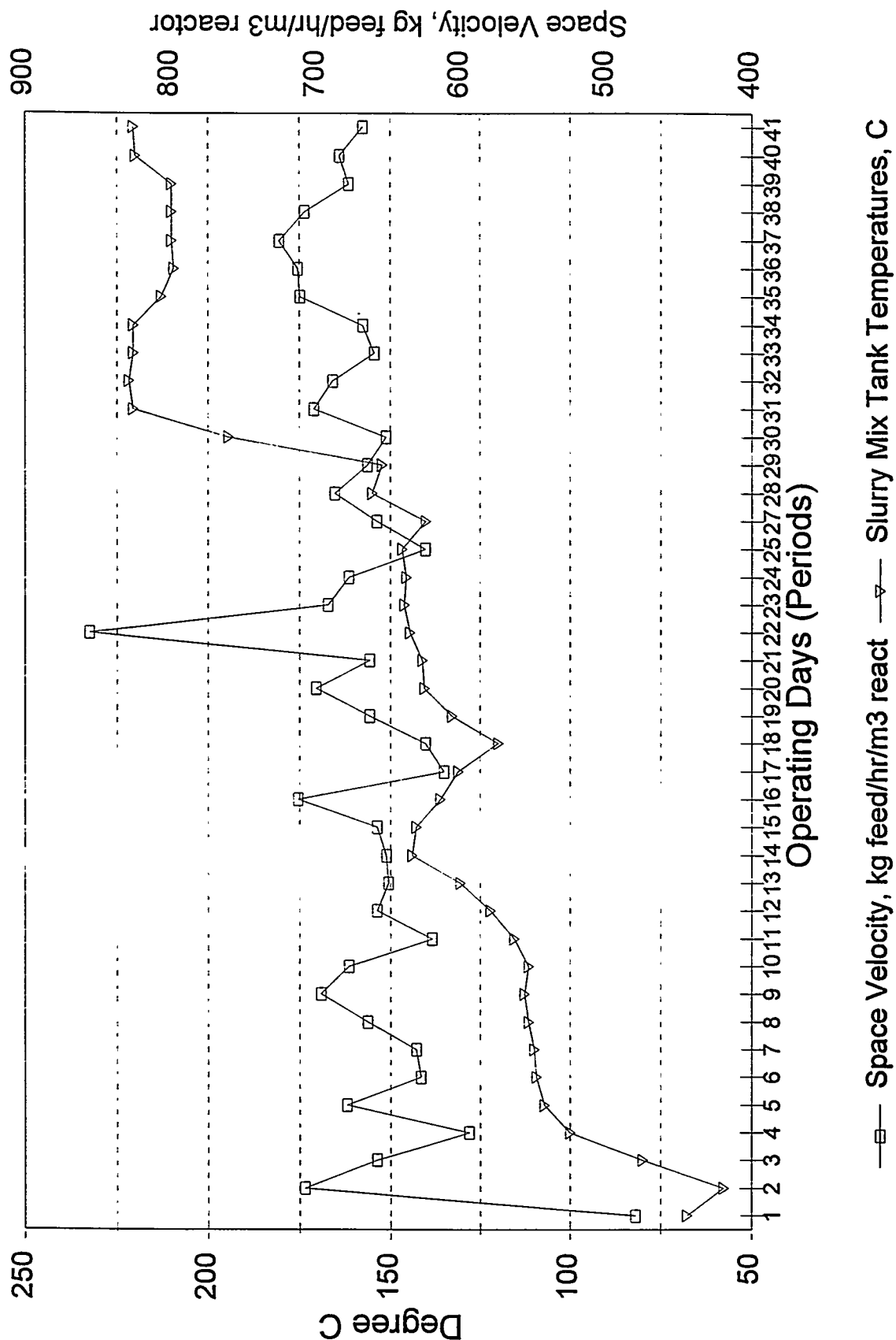
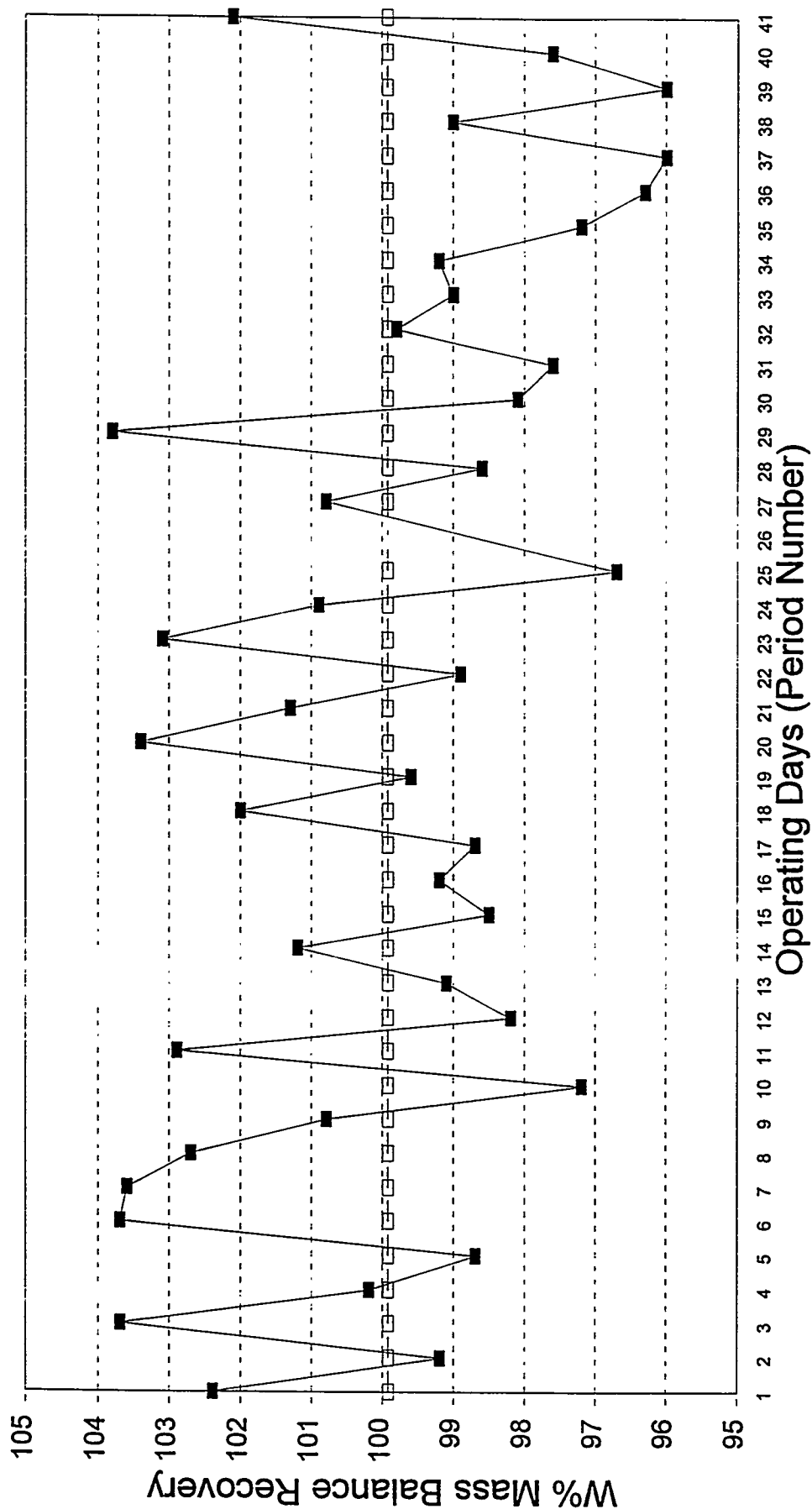


FIGURE 4

CMSL-09: Daily Material Balance



—■— Daily Recovery -□- Average Recovery

FIGURE 5

CMSL-09: Recycle Solvent Balance

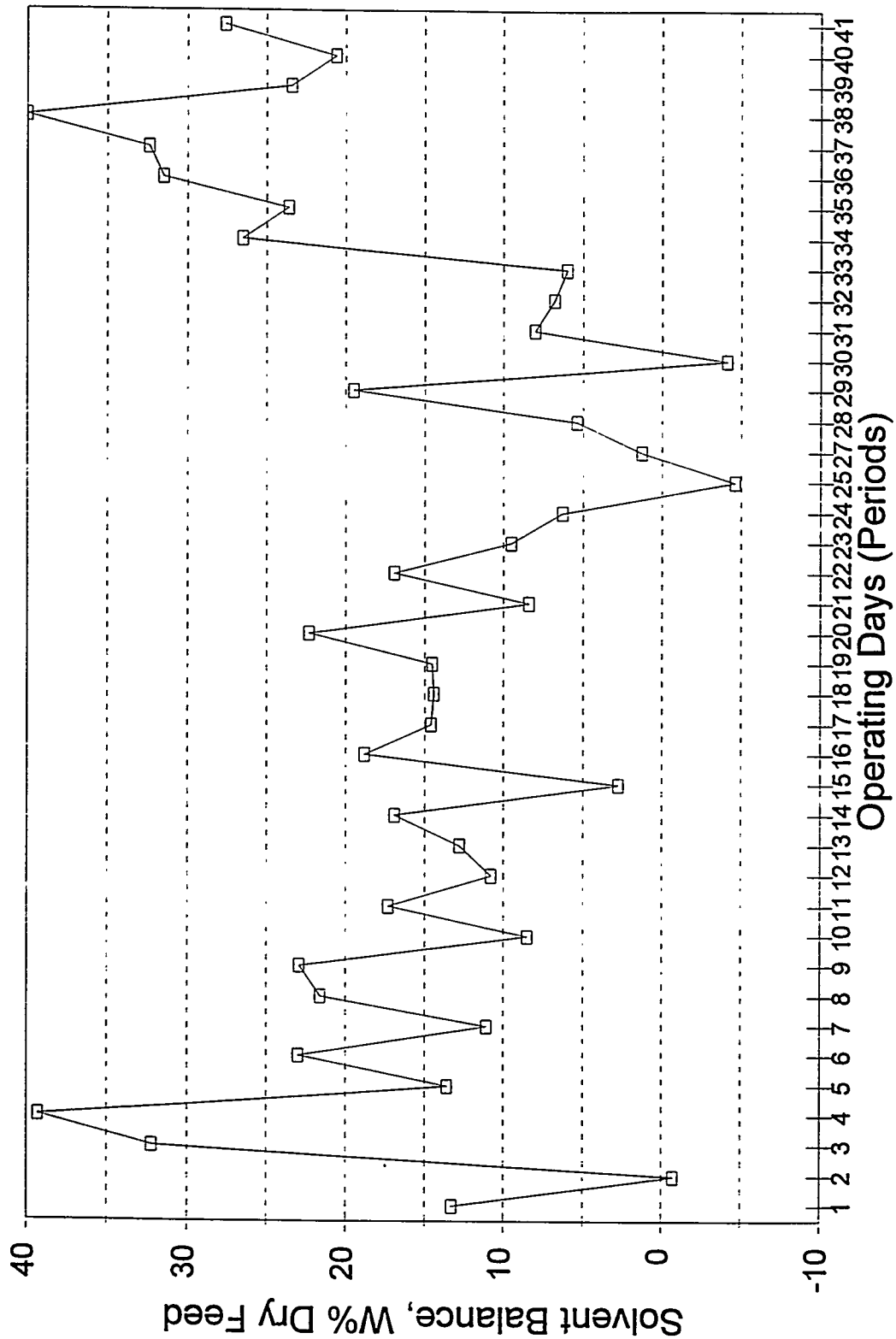


FIGURE 6

CMSL-09 : Feed & Resid Conversions

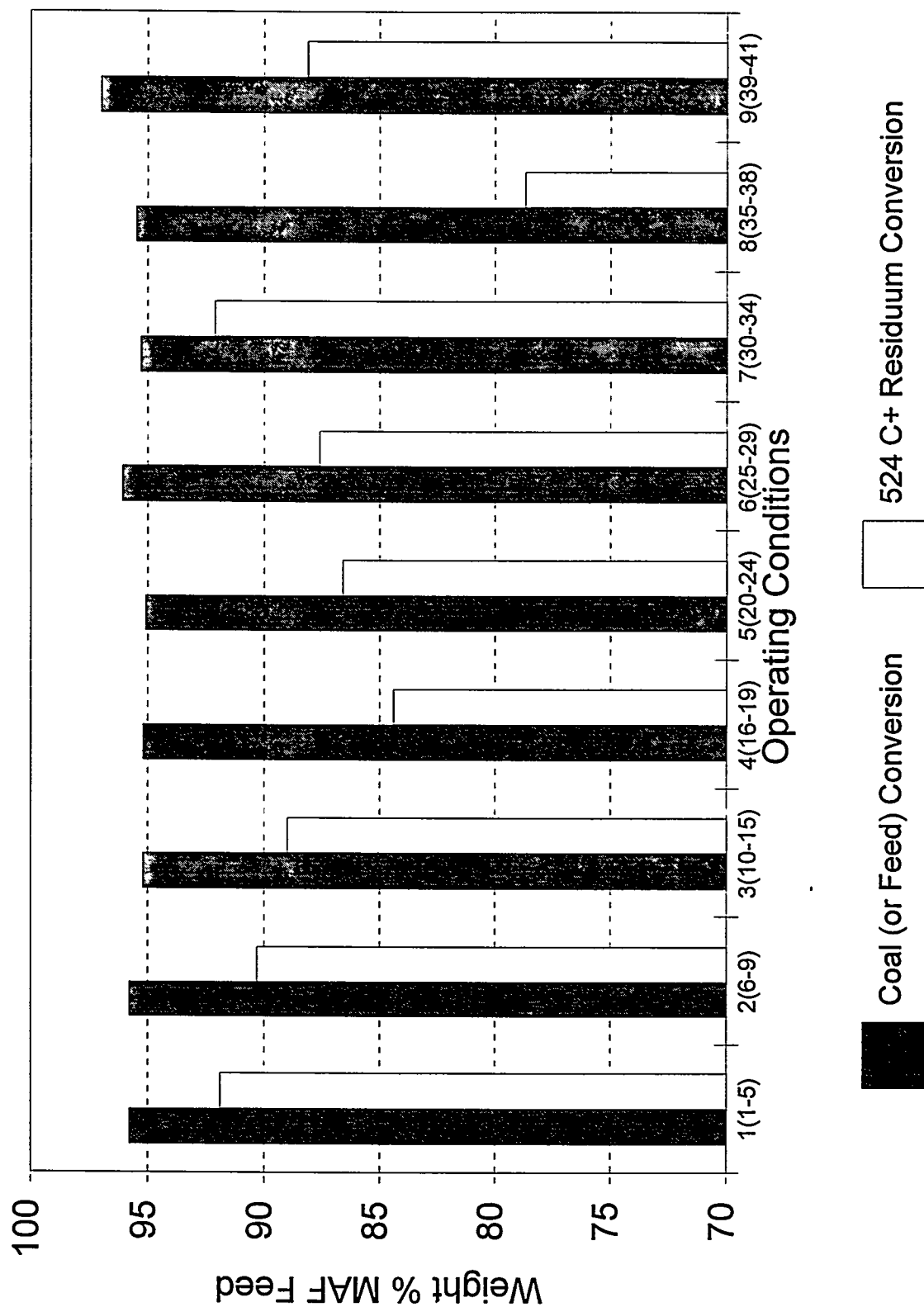


FIGURE 7

CMSL-09: C4-524 C Distillate Yields

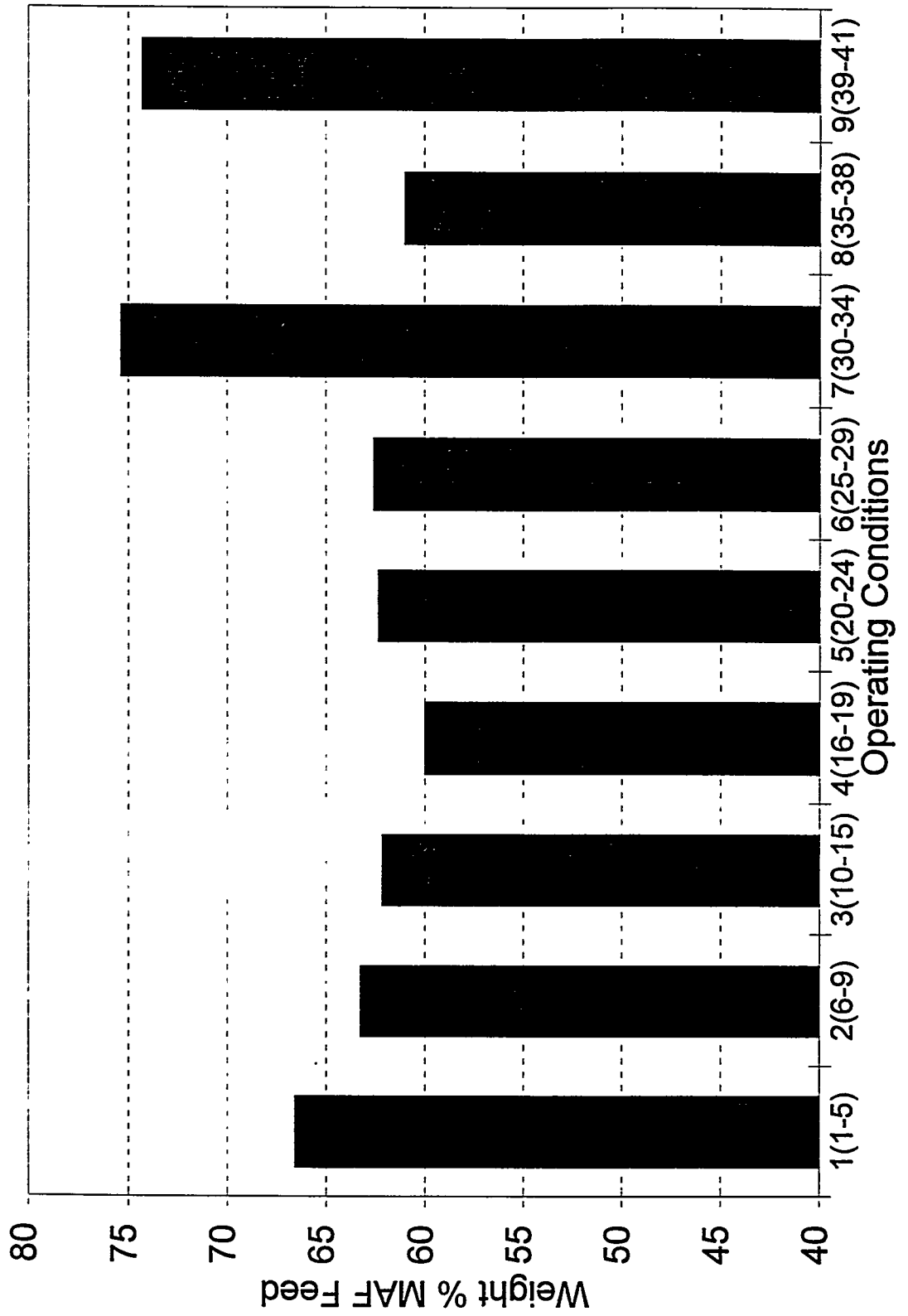


FIGURE 8

CMSL-09 : Distillate Selectivity

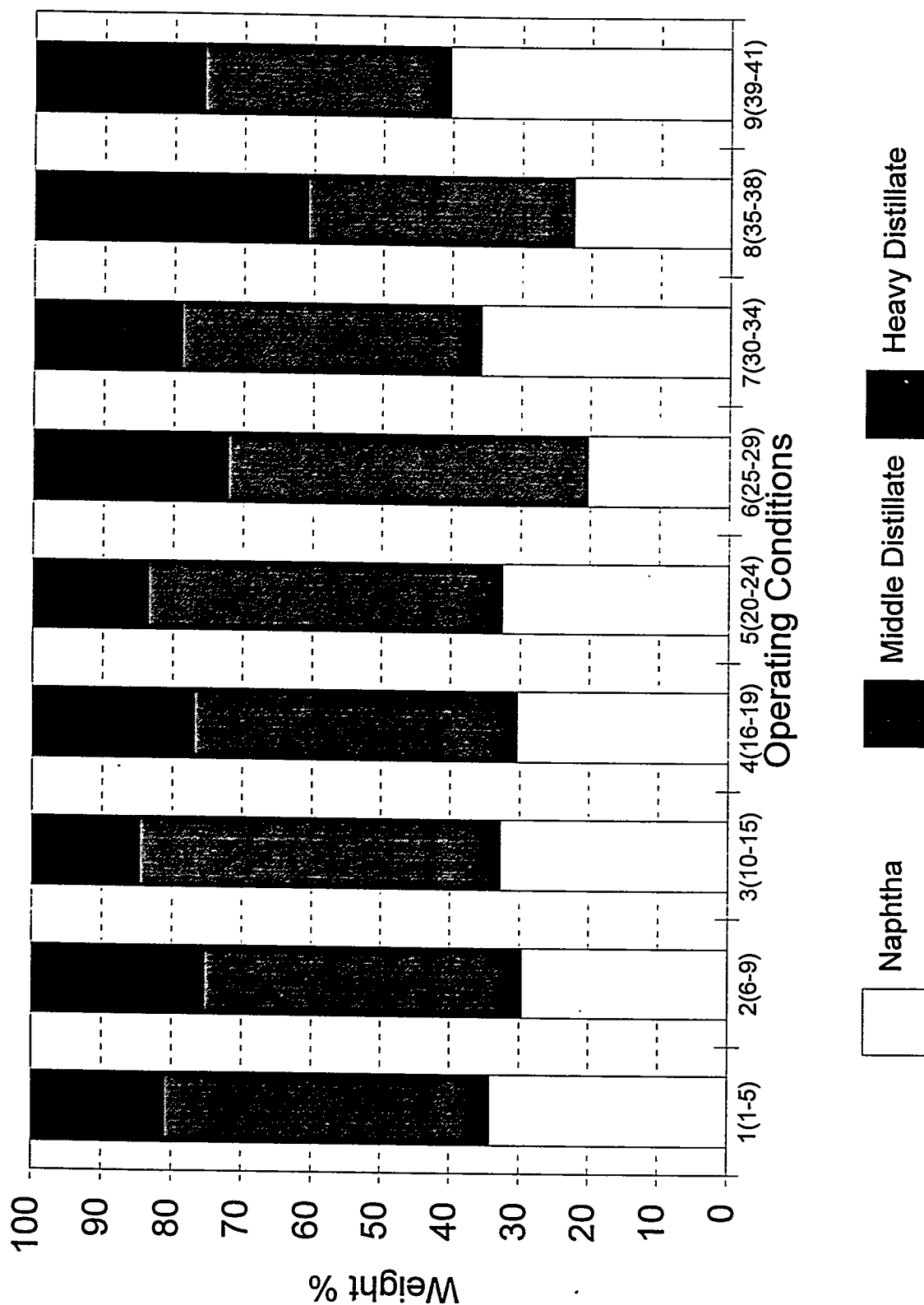


FIGURE 9

CMSL-09: Yields, Dry Feed Basis

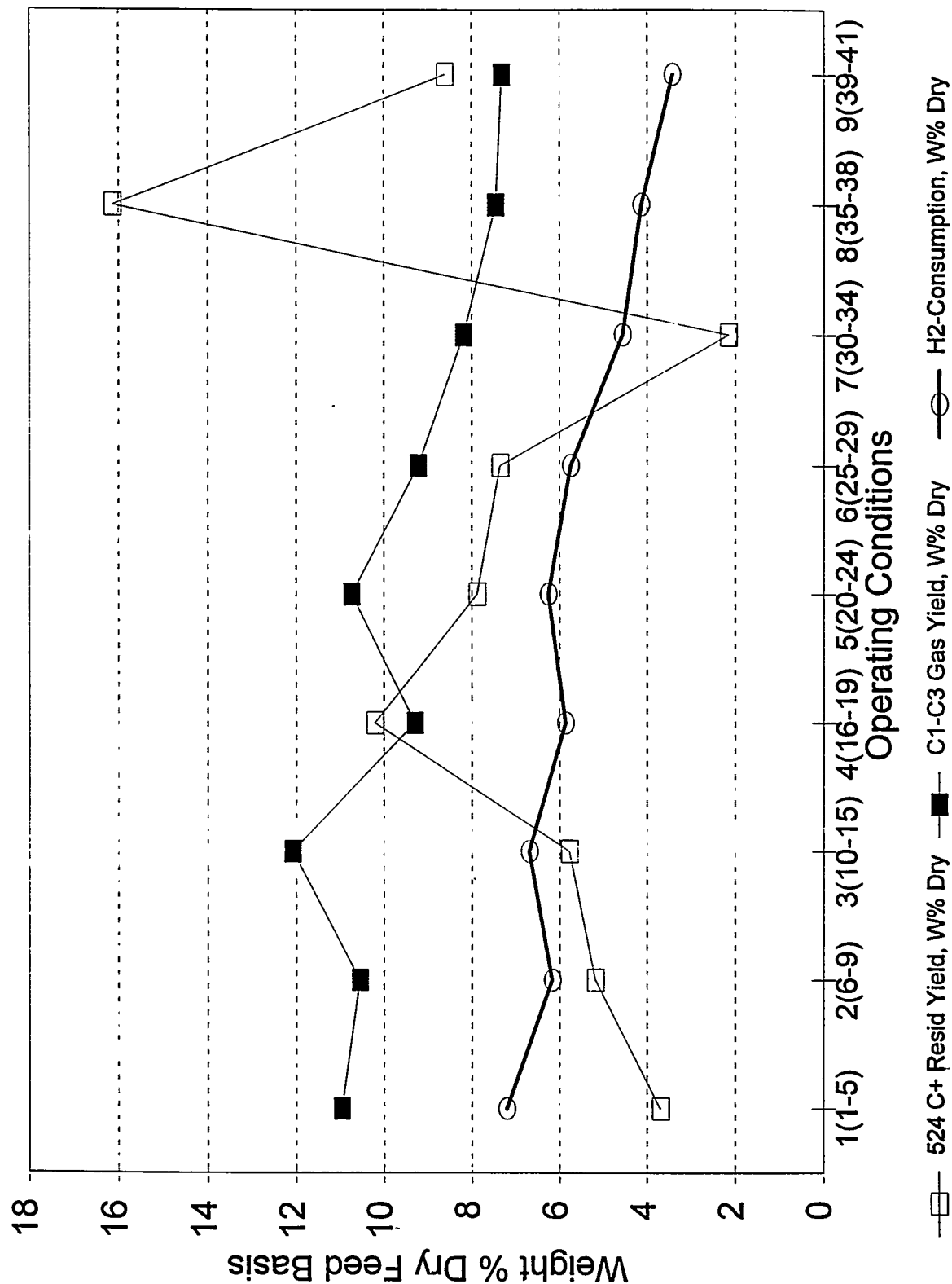


FIGURE 10

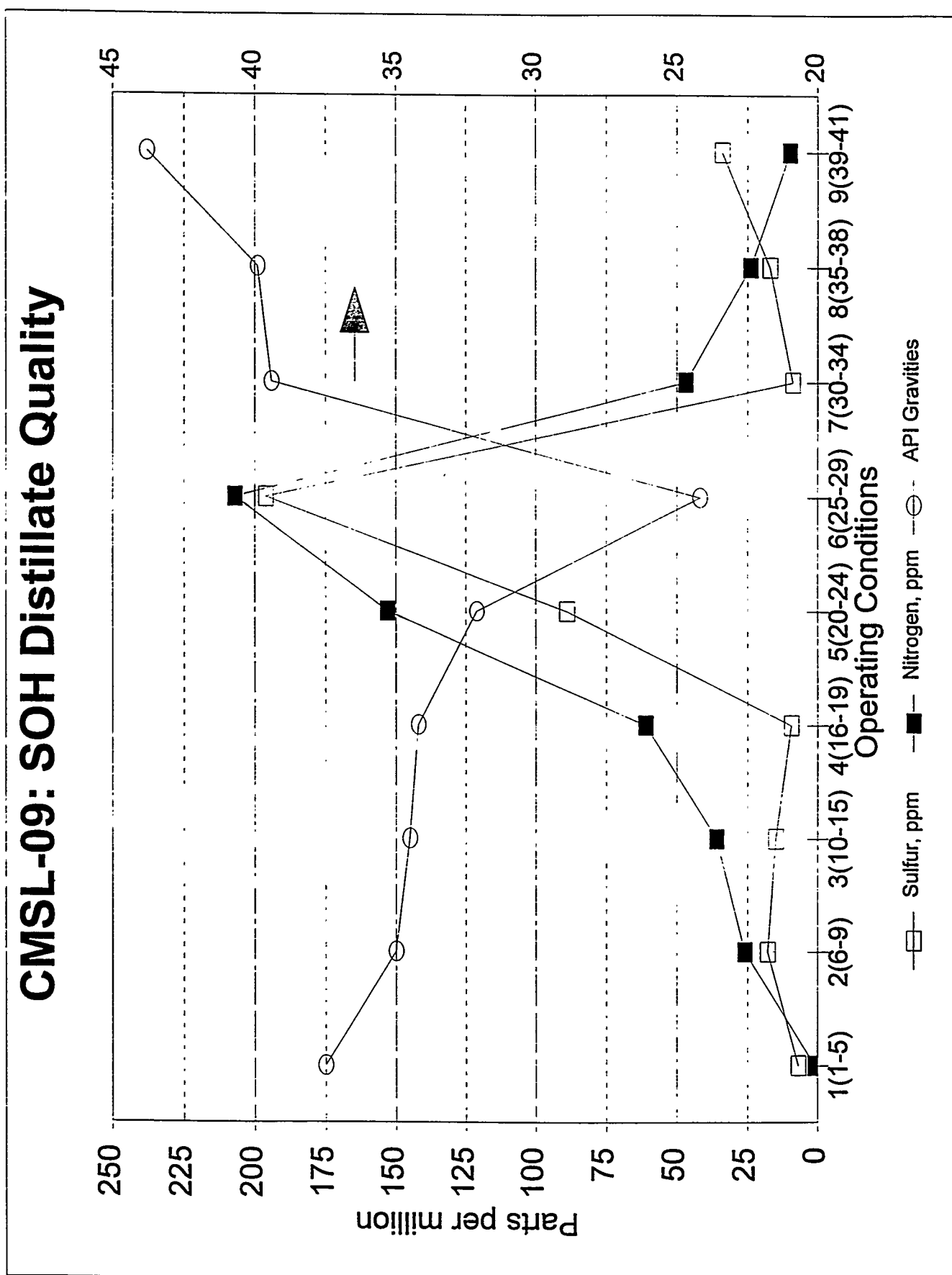
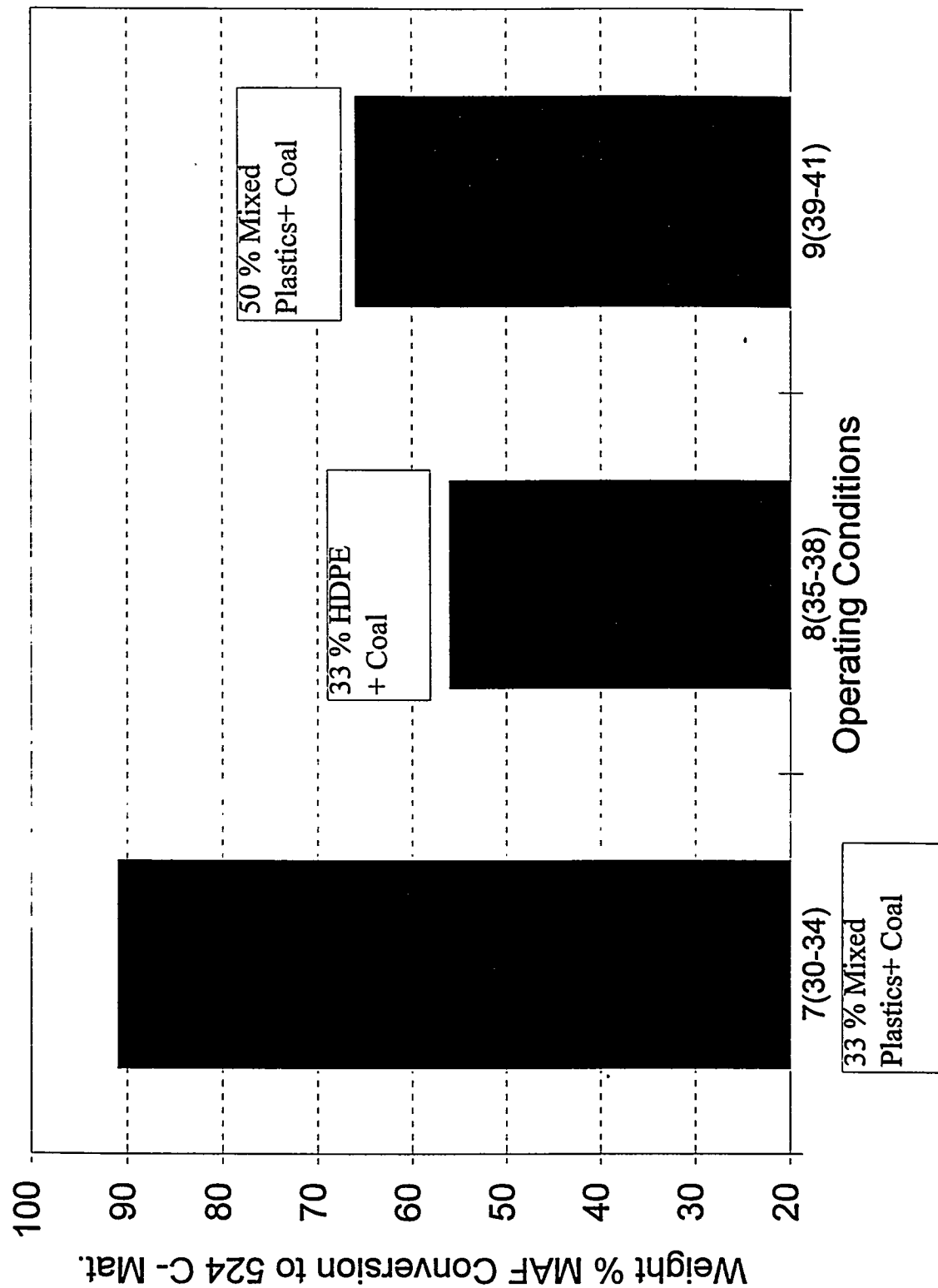


FIGURE 11

CMSL-09: Estimated HDPE Conversion to 524 C- Materials, w%



RUN CMSL-10 (227-88)

EVALUATION OF A COMBINED IRON-MOLYBDENUM DISPERSED SLURRY CATALYST SYSTEM FOR LIQUEFACTION OF BLACK THUNDER MINE COAL

SUMMARY

Bench Run CMSL-10 (HTI Run 227-88) was designed as a follow-up study after Bench Run CMSL-09. During CMSL-09, for the first time at HTI, an all dispersed (slurry) catalyst reactor system was used for coal liquefaction and coal/waste plastics coprocessing. Interestingly, the performance of the multi-stage coal liquefaction unit, under suitable reaction severity with an in-line hydrotreater, was found to surpass the earlier process performance using ebullated bed reactors with supported catalysts. This result was very significant, as dispersed slurry catalysts based on iron and molybdenum, are not only more economical to use than supported catalysts, but they also have tremendous potential to lower overall operational costs for coal liquefaction by elimination of the expensive ebullated bed reactors. The effects of iron-based HTI proprietary catalyst and molybdenum, added as Molyvan-A, were not fully understood during CMSL-09. One of the main objectives of CMSL-10 was to further our understanding of the effects of iron and molybdenum employed alone and added together on process performance. The mode of addition of HTI's iron catalyst and process severity (reactor temperatures and space velocity) were among the variables studied during CMSL-10.

The entire run was spread over 16 days of continuous operations. Because of a shut-down at the beginning of the run, brought about by a high pressure drop in the low-temperature (300°C) pretreater reactor, the actual run spanned Periods 3 to 18. Overall, four conditions were studied during this run: Condition 1 studied the effects of adding 0.5 w% of HTI's iron catalyst in dry, powdered form at a coal space velocity of 640 and reactor temperatures of 441 and 449°C, respectively. Condition 2 looked at the effect of adding 100 ppm molybdenum as Molyvan-A, together with iron, on process performance. Unfortunately, due to resid build up in the recycle solvent, coal space velocity had to be reduced to below 480 kg/h/m³ reactor. In conditions 3 and 4, a wet iron catalyst cake was used as the source of iron at 0.5 w% relative to feed coal and 100 ppm molybdenum from Molyvan-A. In Condition 3, space velocity was back to 640, kg/h/m³ while in Condition 4, space velocity was increased to about 800 kg/hr/m³ reactor. To counter the increased space velocity, reactor temperatures were raised to 449 and 460°C for reactors K-1 and K-2 respectively.

In general, light hydrocarbon gas yields during this run were on the high side (11-16% maf coal); maf coal conversion varied between about 92 to 96 w%. First stage (interstage) maf coal conversion levels were between 91-93.5 w%. Resid conversion varied between 83-91 w% maf, while the yields of light distillates varied between about 57 to 64 w% maf coal. It was evident from Condition 1 that, under the prevailing operating conditions, iron alone at 0.5 w% was not a great catalyst, giving an ordinary performance, i.e., 57% distillate yield, 83% resid conversion, and 92% total coal conversion (all maf bases). After reducing the space velocity and adding

100 ppm of molybdenum, (Condition 2, the process performance improved considerably to, about 64% distillates, 90% + resid conversion, and 94+% total coal conversion. A further increase in space velocity back to 640 (similar to Condition 1) reduced yields and conversion, although these were distinctly higher than those obtained during Condition 1. This proves the utility of molybdenum as a co-catalyst with iron; also it can be said that changing the mode of addition of HTI's iron catalyst did not make any difference in its catalytic function/activity. This point is important because in the new mode of addition of HTI's iron catalyst, two major processing steps in the catalyst synthesis could be eliminated completely, bringing about substantial reduction in the cost of dispersed catalyst. The last run Condition, Condition 4, was made with increased space velocity and increased reactor temperatures, giving marginally better overall performance than Condition 3. Thus, the operability of the unit at high coal throughputs was successfully demonstrated..

BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

Bench Run CMSL-10 was carried out, as a follow-up to CMSL-09, using a dispersed catalyst-only, two-stage, backmixed reactor system. The two conversion reactors were preceded by a back-mixed pretreatment reactor at lower temperature and half the capacity (volume) of each of the conversion reactors. The pretreatment reactor was intended for sulfidation/activation of the dispersed catalyst additive. Bench Run CMSL-10 was eighteen days long, comprising four operating conditions (3-5 days each). The objectives of this bench operation were:

- To determine process performance for a subbituminous coal liquefaction using a three-stage (including pre-treater) dispersed catalyst-only back-mixed reactor system.
- To investigate the effects of a combined catalytic system of molybdenum and iron on process performance.
- To determine the effects of process severity (temperatures and space velocities) on performance.
- To determine the effects of the mode of addition of HTI's iron catalyst process performance.

An in-line hydrotreater was used during this run. Both hot separator (O-1) overheads and atmospheric still overheads (ASOH) were sent through the hydrotreater.

The run plan (Table 14) included four run conditions that were selected to meet the technical objectives specified above. By not using a supported extrudate catalyst in any of the coal liquefaction reactors, it became possible to compare the process performance of different run conditions on a one-to-one basis without being affected by 'catalyst batch-deactivation' phenomenon typical of bench CTSL operations. Condition 1 studied the effects of adding 0.5 w% of HTI's iron catalyst in dry, powdered form on process performance at a coal space velocity of 640 kg/h/m³ and reactor temperatures of 441 and 449°C, respectively. Condition 2 looked at the

effect of adding 100 ppm molybdenum as Molyvan-A, together with iron, on process performance. Unfortunately, due to resid build up in the recycle solvent, the coal space velocity had to be reduced to below 480 kg/h/m³ reactor. Conditions 3 and 4 used a wet iron catalyst cake as the source of iron at 0.5 w% relative to feed coal plus 100 ppm molybdenum from Molyvan-A. In Condition 3 the space velocity was back to 640 kg/h/m³, while in Condition 4 space velocity was increased to about 800 kg/h/m³ reactor. To counter the increased space velocity, reactor temperatures were raised to 449 and 460°C for reactors K-1 and K-2, respectively.

SYSTEM CONFIGURATION:

CMSL-10 involved two equal volume backmixed reactors, one half volume (1000 cc) pretreatment vessel (also backmixed), and a fixed-bed hydrotreater. High pressure slurry samples were obtained both after the pretreatment vessel and after the first conversion reactor. A simplified schematic of this configuration is shown in Figure 12.

The reactors from the existing units 227 and 238 were used in this run with the necessary repiping and equipment modifications. A hot-slurry mix tank system was used throughout the run for slurry preparation. No supported catalyst was used in any of the conversion reactors, except in the hydrotreater (HTU). Hydrogen sulfide (H₂S), as the source of sulfur for activation of the dispersed iron and molybdenum additives, was continually added to the pretreater at 3 w% of dry coal.

COAL FEED, STARTUP AND MAKEUP OIL

Subbituminous Black Thunder Mine Coal (HRI-6213), the same coal that was used in PDU 260-005 (POC-02 Run), was used for CMSL-10 (227-88). Tank 4 material (L-814), a combination of hydrotreated petroleum-derived oil with small amounts of coal-derived liquid obtained during POC-02 was used as startup and makeup oil. The same combination of feed coal and make-up oil was employed during CMSL-09.

CATALYST

Hydrotreater:

Pretreater (carried over to K-1 and K-2):

Criterion C-411 Trilobe (HRI-6135)
Molyvan-A, HTI's Fe Catalyst, and 3
% H₂S relative to dry coal.

OPERATIONAL DETAILS

Bench run CMSL-10 consisted of four run conditions. For the entire run, an average material recovery balance of 101.1W% was achieved. A summary of the material balance on a daily basis is plotted in Figure 13. Since the major objective of CMSL-10 was to study the effects of combined Mo/ Fe catalysts and space velocity on the conversion of coal, this run was originally planned to operate at constant temperature and pressure. Reactor space velocities, and temperatures during CMSL-10 are summarized in Figure 14. Space velocity was adjusted between 415 and 731 kg/h/m³ to examine its impact on process performance. The viscosity of the feed slurry was measured throughout the run and no significant change that might affect pumpability was observed. Unit back pressures were controlled and recorded on an hourly basis. Process operation was similar to run CMSL-9 except that no CAS bottoms was recycled and no ASOH sample was taken during run CMSL-10. Operating conditions and process performance during CMSL-10 are summarized in Table 15. Dispersed catalyst concentrations for different run conditions are shown in Figure 15.

PROCESS PERFORMANCE

TOTAL COAL CONVERSION

Total coal conversion is calculated on the basis of the solubility of pressure filter solids in quinoline. Coal conversions for different conditions are shown in Figure 16. Throughout the course of Run 227-88, coal conversion varied between 92 W% and 96 W%, maf. Only FeOOH/SO₄ catalyst was added during Periods 3-6 of condition 1. Coal conversion during these periods was used as a baseline to compare with the performance of combined Mo/Fe catalysts. Starting from period 7 of Condition 2, 100 ppm Molyvan-A catalyst was added to the process. As shown in Figure 16, the addition of Molyvan-A catalyst resulted in an increase in total conversion. At the beginning of condition 3 (Period 11), space velocity was slightly increased. The increase in space velocity did not significantly affect feed conversion. During the last two conditions (Period 11 through 18), FeOOH/ SO₄ catalyst containing 70 W% water (i.e., in the form of a wet filter cake) was added in an amount equivalent to dry FeOOH/ SO₄ used previously. An interesting finding was that iron catalyst, added either as dry powder or wet cake, has the same positive effect on coal conversion. This is a significant finding, as it will not only reduce the cost of iron catalyst but also help in understanding the catalytic action of FeOOH/SO₄ catalyst in coal liquefaction.

524°C+ RESIDUUM CONVERSION

Resid conversion measures the ability of the process to convert heavy (high boiling) fractions contained in the feed. For the purpose of calculations, all of the maf portion of the feed coal is considered as 524°C+ resid in the feed. 524°C+ resid conversion varied between 82 and 90 W% and was more sensitive to the addition of Molyvan-A catalyst and to changes in space velocity than was total coal conversion. Resid conversion during each condition is shown in Figure 17. A comparison of process performance between conditions 1 and 2 indicates that the addition of 100 ppm (and lowering space velocity from 640 to about 416 kg/h/m³ reactor) caused about a 7 W% increase in 524°C+ resid conversion. To verify the effect of Molyvan-A catalyst on coal conversion, during periods 11-14 of Condition 3 the process was operated under the same space velocity as Condition 1 but with Molyvan-A added. About a 3 W% increase in 524°C+ resid conversion was observed. Residence time of slurry feed affects 524°C+ resid conversion. As shown in Figure 17, 524°C+ resid conversion dropped by about 7 W% when the space velocity was increased from 416 kg/h/m³ (Condition 2) to 731 kg/h/m³ (Condition 4). As indicated above, starting from period 11 of Condition 3, the iron catalyst was added as wet cake (containing 70 % water). The change in FeOOH/SO₄ water content did not have any noticeable influence on resid conversion.

C₄-524°C DISTILLATE YIELDS AND SELECTIVITY

Distillate yields varied between 57 and 64 W%. As shown in Figure 18 and Table 15, the type of catalyst and space velocity affected distillate yields. A trend similar to that for the resid conversion was observed for distillate yields. The highest distillate yield of 63.6 W% was obtained for Condition 2 100 ppm of Molyvan-A catalyst and reduced space velocity. Distillate yield dropped slightly when the space velocity was increased from 25.9 to 45.7 kg/h/m³. The lowest distillate yield was obtained in condition 1 when FeOOH/SO₄ alone was the dispersed catalyst. An important implication may be that the combined system of Mo and Fe catalysts is effective in upgrading polyaromatic structures and breaking strong C-C bonds in coal. Also shown in Figure 19 is the selectivity of distillates for all conditions. The distillates, in general, contained 30 W% naphtha and 40 W% of middle distillate. Middle distillate (177-343°C) yield followed a trend similar to that for overall distillate yield.

HYDROGEN CONSUMPTION

Hydrogen consumption based on mf feed, varied between 4.4 and 7.5 W%. The highest hydrogen consumption was observed for Condition 2 with Molyvan-A catalyst and reduced space velocity (Figure 20). Middle distillate and gas yield for Condition 2 were also the highest, indicating that extensive hydrocracking occurred. On raising space velocity, the hydrogen consumption decreased together with the reduction in the formation of gases. Lower hydrogen consumption for Condition-4 did not affect distillate yields significantly.

C₁-C₃ GAS YIELDS

As shown in Figure 21, normalized C₁-C₃ gas yield for CMSL-10 varied between 10.9 and 15.7W%. The highest yield (15.7 W%) was obtained during periods 7-9 of Condition 2, with Molyvan-A catalyst and reduced space velocity. It is interesting that the formation of C₁-C₃ gases followed a trend similar to that for hydrogen consumption. Gas yield was reduced during the last condition which was at the highest space velocity. This suggests that the high gas yields can be reduced by reducing residence time.

524°C+ RESIDUUM YIELD

524°C+ residue yields for CMSL-10 varied between 4 and 12 W%, as indicated in Figure 22. The addition of Molyvan-A catalyst reduced the residuum yields due to the strong hydrocracking ability of Molyvan-A catalyst. An increase in residuum yield was observed on raising space velocity.

PRODUCT QUALITY

Various fractions (First-Stage/Second-Stage Vent Gases, CAS Bottoms, SOH, PFL and PFS/VSB) from work-up periods 6,9,14 and 18 were analyzed in detail. The results of these analyses are summarized in Tables 16 through 20.

Separator Overhead Product (SOH)

SOH oil represents the net light distillate (IBP-750°F) from CMSL-10. Properties of SOH oil for the work-up periods are shown in Table 16. SOH oil had a typical boiling range of 54-399°C. The IBP-177°C Fraction, the lightest fraction of the SOH oil, is almost the same for all conditions. The API gravities (an indication of paraffinic character) of the SOH oil for all work-up period were high (>34). The heteroatoms level (nitrogen and sulfur) were below 50 ppm throughout the run, indicating very successful operation of the in-line hydrotreater. The change of space velocity and addition of Molyvan-A catalyst did not affect the SOH distillation.

Pressure Filter Liquid (PFL)

Pressure filter liquid (PFL) represents the liquid (oil) part of the atmospheric still (CAS) bottoms. In CMSL-10, CAS bottoms was not used as recycle solvent; only the solids-free PFL was used as recycle oil. As shown in Table 17, PFL has a broad boiling range. The IBP of the PFL for all conditions is about 243°C. As shown in Figure 23, toluene solubles in the PFL varied from 84 to 94 W%, while cyclohexane soluble varied from 60 to 70 W%. The yield of the high boiling fraction (524°C+) varied from 34 to 46 W%, depending on process conditions. A large portion of the 524°C+ PFL was toluene soluble (70 W%). As shown in Table 17, the yield of the

975°F+ fraction was reduced upon addition of Molyvan-A catalyst. Space velocity also positively affected the 524°C+ content of the PFL. The addition of Molyvan-A catalyst resulted in an increase in the H/C ratio, indicating that Molyvan-A catalyst has a good hydrogenation function.

INTERSTAGE SAMPLES

Interstage samples were withdrawn from the ebullating line on the first stage coal liquefaction reactor. The properties of these samples shed light on the performance of the first stage reactor. Interstage samples of the product slurry from the first stage reactor were collected during all the work-up periods of CMSL-10 (Tables 19 and 20). The pressure filter solids from the first stage were analyzed, and it indicated that 91-93.5 W% maf of coal conversion was achieved after the first stage. The toluene soluble portion of the 524°C+ fraction is about 80 W%. The overall resid content of the PFL varied between 36-45 w%. Comparison between Periods 14 and 18 interstage PFL analyses indicates that increased space velocity did not affect PFL quality significantly.

EXTERNAL SAMPLES

As mentioned earlier, a number of samples of various process streams were obtained (for further detailed characterization and products assessment) for the Consol, Inc. and for members of the Consortium of Fossil Fuel Liquefaction Science. These samples, their amounts, and the operating periods when these were withdrawn are shown in Table 21.

CONCLUSIONS

After 18 periods of continuous operation, CMSL-10 was successfully completed with one brief shut-down. The results demonstrated that the combination of Mo and FeOOH catalysts improved process performance. (Iron alone was not very effective a catalyst.) It was found that process performance remained the same whether iron catalyst (FeOOH/SO_4) was added dry or as wet cake containing 70 W% water. This discovery should reduce catalyst costs by 30% due to the elimination of two time consuming and expensive processing steps in catalyst preparation. Space velocity and catalyst type had an impact on 524°C+ conversion and distillate yield but did not seem to affect total conversion. A slight change in the quality of SOH and PFL was observed upon changing space velocity. This suggests that the process can be operated at even higher throughput. In-line hydrotreating was very effective for the removal of heteroatoms and for hydrogenation. The use of an in-line hydrotreater has resulted in the production of high quality distillates which contain less than 50 ppm each of sulfur and nitrogen. Analysis of samples from various process streams indicated that the current reactor configuration and combined system of Mo and Fe catalysts are effective in producing quality products from coal liquefaction. It is possible to establish an effective process for coal liquefaction using a suitable combination of iron and molybdenum in low concentrations (5000 ppm for iron and 50-100 ppm for molybdenum) so that these dispersed catalysts can be employed on a disposable basis.

RECOMMENDATIONS FOR FUTURE WORK

Based upon the results from bench runs CMSL-09 and CMSL-10, it is strongly recommended that a slurry catalyst system, comprising iron and molybdenum, be optimized. In the past two bench runs, iron and molybdenum were added from different sources; it will be interesting to determine how well a bimetallic catalyst additive, consisting of both iron and molybdenum in the same formulation, performance under comparable process conditions. The HTI's iron catalyst preparation is easily amenable for incorporation of any other metal(s) into the catalyst formulation. For the first time during CMSL-10, it was found that a wet filter cake consisting of about 70% water is almost as effective as the dried form of the iron catalyst. Wet cake catalyst addition, which is much more economical than the dry powder addition, should be looked into in more detail and should be optimized. The iron-molybdenum dispersed catalyst combination should be studied for coprocessing of coal with heavy resids and waste organics (plastics).

TABLE 14

CMSL-10 OPERATING CONDITIONS

Black Thunder Coal (HRI-6213: POC-02 coal, dried to about 11% moisture)

Back Pressure: 2500 psig

Catalyst: Dispersed Fe and Mo Catalysts & C-411 in HTU

Condition	1	2	3	4
Periods	3-6	7-9	10-14	15-18
Dates	06/13-16/95	06/17-19/1995	06/20-25/95	06/26-29/95
Work-up Periods	5	9	14	18
Temperatures, C				
Pretreater	300	300	300	300
Reactor K-1	440	440	440	449
Reactor K-2	449	449	449	460
Hydrotreater	379	379	379	379
Space Velocity, kg coal/h/m ³ reactor	640	480	640	800
Solvent/Coal Ratio	1	1	1	1
Dispersed Catalysts, ppm				
HTI Fe Catalyst	5000	5000	5000	5000
Molyvan-A	0	100	100	100
Recycle	PFL	PFL	PFL	PFL
H ₂ S Additive, w% dry coal	3	3	3	3

TABLE 15

CMSL-10: PROCESS PERFORMANCE SUMMARY

Unit	227	227	227	227
Run	88	88	88	88
Condition	1	2	3	4
Period Number	6	9	14	18
Hours of Run (end of Period)	144	216	336	432
Disp. Cat. ppm*: Fresh Mo	0	100	100	100
Fresh Iron	5000	5000	5000	5000
Stage I Feed Space Velocity kg coal/hr/m3 reactor vol.	659.2	414.4	654.4	731.2
Temperatures, C				
Pretreater	303	302	304	302
K-1	443	441	444	449
K-2	450	448	451	457
Total Material Recovery % (Gross)	100.2	103.5	102.2	100.9
ESTIMATED NORMALIZED YIELDS:				
W% DRY Coal				
C1-C3 in Gases	13.37	15.71	12.20	10.95
C4-C7 in Gases	4.35	5.63	4.56	3.79
IBP-177 deg C	12.35	15.78	12.81	12.75
177-260 deg C	10.61	11.70	9.69	11.13
260-343 deg C	11.67	15.79	13.96	13.73
343-454 deg C	11.84	9.50	12.73	13.21
454-524 deg C	2.65	1.55	3.39	4.02
524 deg C+	8.76	4.00	8.60	11.52
Unconverted Feed	7.66	5.34	5.16	3.26
Water	10.91	10.41	10.96	9.27
- COx	5.68	5.36	5.63	3.89
NH3	0.87	1.03	0.86	0.73
H2S	-0.17	-0.08	-0.19	0.08
Hydrogen Consumption	6.30	7.45	6.12	4.09

PROCESS PERFORMANCE, maf Coal

Coal Conversion	91.9	94.3	94.5	96.5
524 C+ Conversion	82.5	90.1	85.4	84.0
C4-524 C Distillate Yield	56.7	63.6	60.6	62.2

*The first two run conditions employed a dry/powdered form of iron catalyst, while the last two employed iron catalyst in the form of a wet filter cake.

TABLE 16

CMSL-10: SEPARATOR OVERHEAD (SOH) PROPERTIES

Unit	227	227	227	227
Run	88	88	88	88
Condition	1	2	3	4
Period Number	6	9	14	18
Gravity, API	38	34	35.9	35.4
IBP, deg C	60.0	55.0	55.0	53.9
FBP, deg C	372.2	378.9	375.6	363.3
ASTM D-86 Distillation, Composition				
W % IBP-177 deg C	35.2	33.5	35.5	35.8
W% 177-260 deg C	27.9	25	26.4	30.2
W% 260-343 deg C	25.2	31.1	28.8	26.7
W% 343 deg C+	10.8	9.7	8.5	7.2
W% Loss	0.9	0.7	0.8	0.1
Elemental Analysis				
Carbon, W%	86.42	87.2	86.84	87.22
Hydrogen, W%	13.44	12.75	12.96	12.59
Sulfur (Antek), ppm	10.6	53	46	29
Nitrogen (Antek), ppm	<0.5	55	53	63
H/C RATIO	1.87	1.75	1.79	1.73

TABLE 17

CMSL-10: PROPERTIES OF THE PRESSURE FILTER LIQUID (2nd STAGE)

Unit	227	227	227	227
Run	88	88	88	88
Condition	1	2	3	4
Period Number	6	9	14	18
Gravity, API	-12.3	-6.5	-5.4	-11.9
IBP, deg C	247.2	244.4	234.4	233.9
ASTM D-1160 Distillation, Composition				
W % IBP-177 deg C	7.1	11.2	14.1	12.5
W% 177-260 deg C	32.4	41.2	37.3	32.5
W% 260-343 deg C	13.7	12.9	13.5	12.6
W% 343 deg C+	46.2	33.9	34.2	41.6
W% Loss	0.6	0.8	0.9	0.8
Elemental Analysis				
Carbon, W%	88.6	88.6	88.4	84.7
Hydrogen, W%	6.4	7.0	7.3	6.9
Sulfur, W%	0.9	0.7	0.5	0.7
Nitrogen, W%	0.9	0.9	0.9	1.0
H/C RATIO	0.9	0.9	1.0	1.0
CCR, W% PFL	33.8	22.4	20.5	25.0
CYCLOHEXANE INSOLUBLES, W%	41.1	22.0	23.1	30.9
TOLUENE INSOLBLES, W%	16.5	7.3	5.9	14.4

TABLE 18

CMSL-10: INSPECTION, OF THE PRESSURE FILTER SOLIDS (2nd STAGE)

Unit	227	227	227	227
Run	88	88	88	88
Condition	1	2	3	4
Period Number	6	9	14	18
Elemental Analysis				
Carbon, W%	65.3	60.7	57.7	48.9
Hydrogen, W%	3.8	4.1	3.8	3.4
Sulfur, W%	2.0	2.0	2.3	2.3
Nitrogen, W%	0.7	0.6	0.6	0.5
H/C RATIO	0.7	0.8	0.8	0.8
Composition, W%				
Quinoline Insolubles, w%	50.6	50.2	53.8	61.6
Ash (Quinoline Filtration)	24.6	29.4	32.4	41.8
S in Ash, w%	4.8	4.7	5.0	5.0
ASTM Ash, W%	25.8	30.4	33.8	42.0
S in Ash, W%	5.5	5.0	5.7	5.8
Fe in Ash, w%				
Mo in Ash, w%				
Coal Conversion, w% maf	91.9	94.3	94.5	96.5

TABLE 19

CMSL-10: PROPERTIES OF THE FIRST STAGE PRESSURE FILTER LIQUID

Unit	227	227	227
Run	88	88	88
Condition	2	3	4
Period Number*	9	14	18
Gravity, API	-5.6	-7.9	-8.9
IBP, deg C	234.4	265.6	255.0
ASTM D-1160 Distillation, Composition			
W % IBP-177 deg C	11.9	6.9	8.7
W% 177-260 deg C	34.3	32.8	32.2
W% 260-343 deg C	16.9	14.4	14.2
W% 343 deg C+	36.3	45.3	44.3
W% Loss	0.6	0.6	0.6
Elemental Analysis			
Carbon, W%	89.2	88.9	89.2
Hydrogen, W%	7.3	6.7	7.1
Sulfur, W%	0.7	0.5	0.5
Nitrogen, W%	0.8	1.1	1.0
H/C RATIO	1.0	0.9	1.0
CCR, W% PFL	23.0	26.2	28.8
CYCLOHEXANE INSOLUBLES, W%	25.9	30.5	37.0
TOLUENE INSOLBLES, W%	8.0	9.1	9.1

*Period 6 interstage sample could not be pressure filtered due to its highly viscous nature.

TABLE 20

CMSL-10: INSPECTION OF THE FIRST STAGE PRESSURE FILTER SOLIDS

Unit	227	227	227
Run	88	88	88
Condition	2	3	4
Period Number	9	14	18
Elemental Analysis			
Carbon, W%	65.3	63.9	54.1
Hydrogen, W%	4.3	4.4	3.9
Sulfur, W%	2.0	2.0	2.0
Nitrogen, W%	0.8	0.8	0.5
H/C RATIO	0.8	0.8	0.9
Composition, W%			
Quinoline Insolubles, W%	50.7	51.1	58.0
Ash (Quinoline Filtration)	23.4	26.6	39.0
ASTM Ash, W%	24.2	26.7	35.7
S in Ash, W%	5.0	5.7	9.0
Coal Conversion, W% maf	91.8	93.0	93.6

TABLE 21

Hydrocarbon Technologies, Inc.

SHIPPING REQUEST FORM

<u>Requested By :</u> Vivek Pradhan	<u>Need Date</u> 07/15/95	<u>WO Number</u> 846-344	<u>Date Sub.</u> 07/07/95																					
<u>Sample Description & Amounts:</u> <div style="float: right;"><u>File with:</u> 227-88</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 40%;">1. FEED SLURRY</td> <td style="width: 20%;">250 GM</td> <td style="width: 40%;">PERIODS 6, 9, 14, 18</td> </tr> <tr> <td>2. CAS BOTTOMS</td> <td>350 GM</td> <td>PERIODS 6, 9, 14, 18</td> </tr> <tr> <td>3. SOH OIL</td> <td>250 GM</td> <td>PERIODS 6, 7, 9, 14, 18</td> </tr> <tr> <td>4. ASOH MATERIAL</td> <td>250 GM</td> <td>PERIODS 6, 7, 9, 14, 18</td> </tr> <tr> <td>5. PRESSURE FILTER LIQUID</td> <td>350 GM</td> <td>PERIODS 6, 9, 14, 18</td> </tr> <tr> <td>6. PRESSURE FILTER SOLID</td> <td>350 GM</td> <td>PERIODS 6, 9, 14, 18</td> </tr> <tr> <td>7. INTERSTAGE (K-2) SLURRY</td> <td>350 GM</td> <td>PERIODS 6, 9, 14, 18</td> </tr> </table>				1. FEED SLURRY	250 GM	PERIODS 6, 9, 14, 18	2. CAS BOTTOMS	350 GM	PERIODS 6, 9, 14, 18	3. SOH OIL	250 GM	PERIODS 6, 7, 9, 14, 18	4. ASOH MATERIAL	250 GM	PERIODS 6, 7, 9, 14, 18	5. PRESSURE FILTER LIQUID	350 GM	PERIODS 6, 9, 14, 18	6. PRESSURE FILTER SOLID	350 GM	PERIODS 6, 9, 14, 18	7. INTERSTAGE (K-2) SLURRY	350 GM	PERIODS 6, 9, 14, 18
1. FEED SLURRY	250 GM	PERIODS 6, 9, 14, 18																						
2. CAS BOTTOMS	350 GM	PERIODS 6, 9, 14, 18																						
3. SOH OIL	250 GM	PERIODS 6, 7, 9, 14, 18																						
4. ASOH MATERIAL	250 GM	PERIODS 6, 7, 9, 14, 18																						
5. PRESSURE FILTER LIQUID	350 GM	PERIODS 6, 9, 14, 18																						
6. PRESSURE FILTER SOLID	350 GM	PERIODS 6, 9, 14, 18																						
7. INTERSTAGE (K-2) SLURRY	350 GM	PERIODS 6, 9, 14, 18																						
<u>Special Instructions:</u> [PLEASE ENCLOSE THE MSDS INFORMATION WITH THE SHIPMENT]																								
<u>WHERE DO SAMPLES GO?</u> Attention: DR. GARY ROBBINS CONSOL, INC. R & D 400 BROWNSVILLE ROAD LIBRARY, PA 15129.																								
<u>AUTHORIZED:</u> (THEO L. K. LEE)																								

FIGURE 12

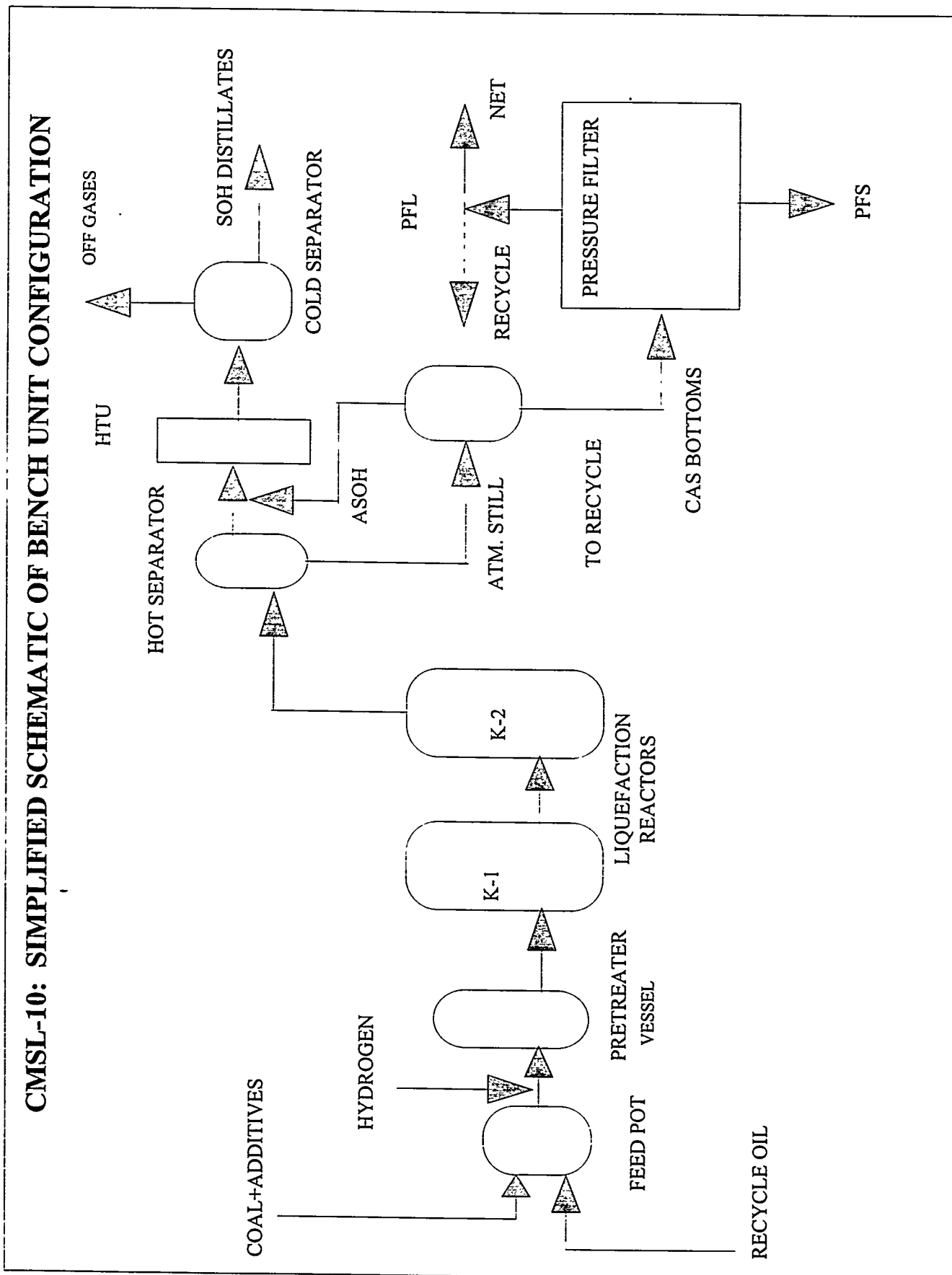


FIGURE 13

CMSL-10: Daily Material Balance

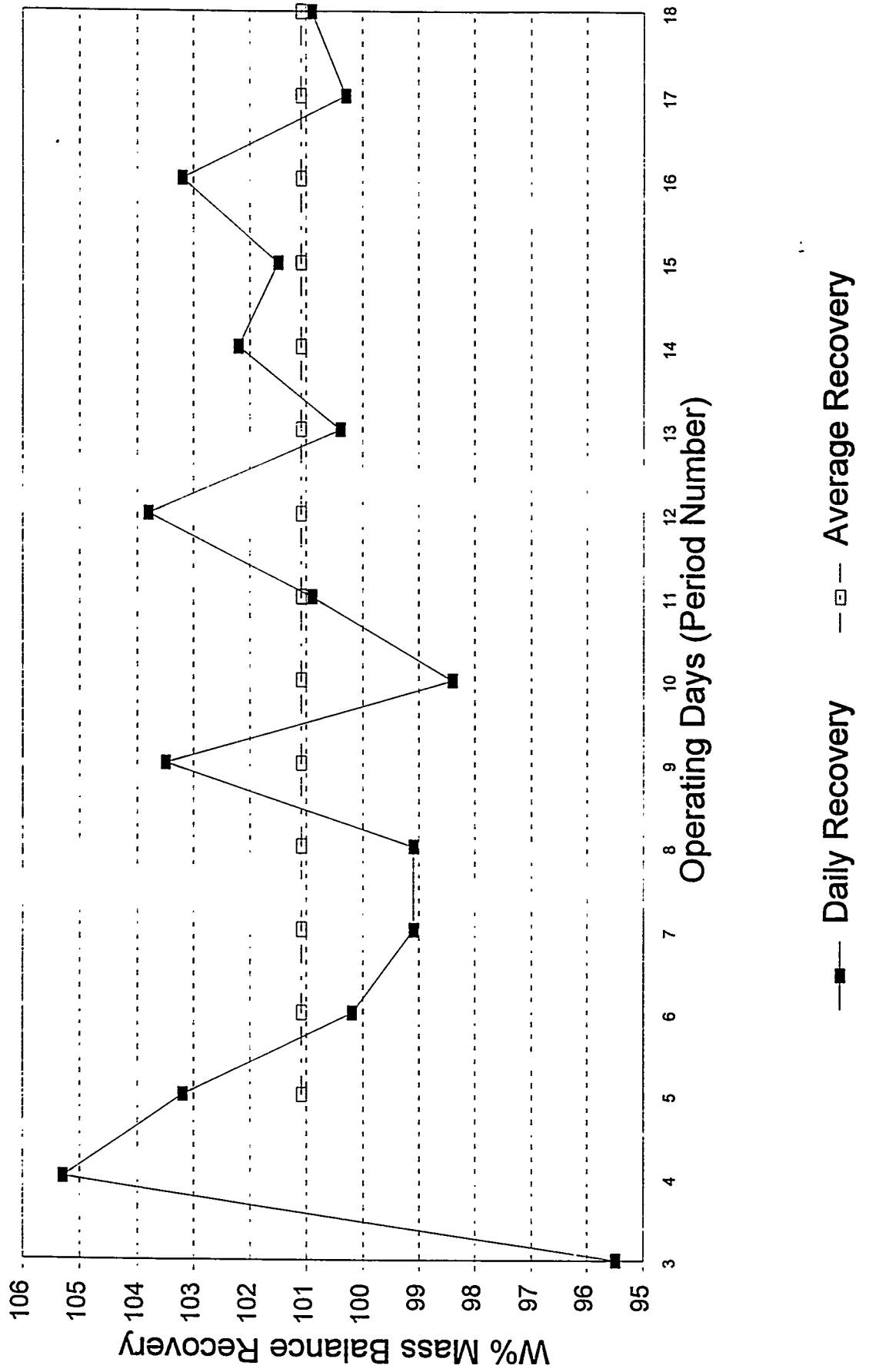
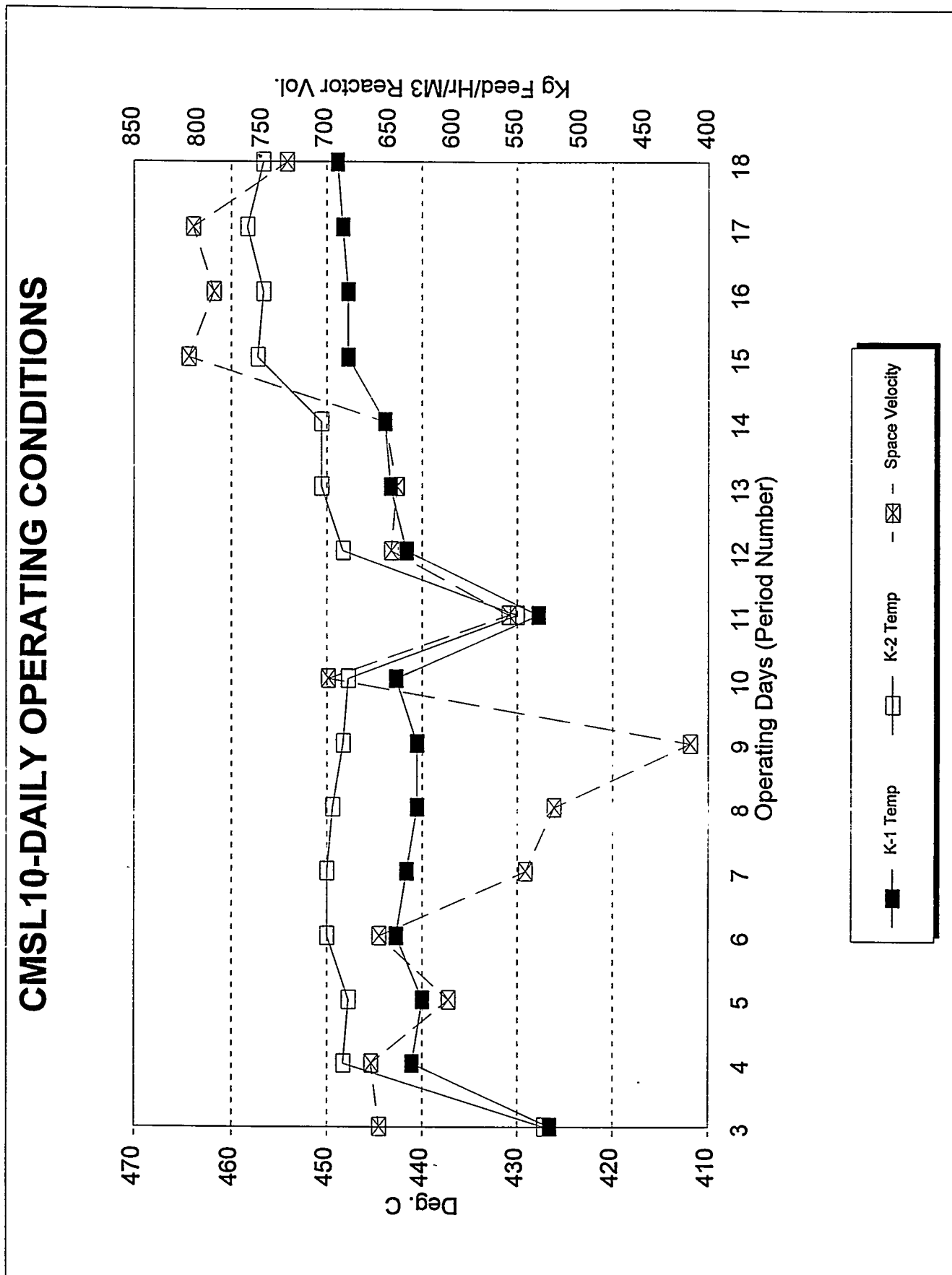


FIGURE 14



CMSL-10: Dispersed Catalysis

Catalyst Loading

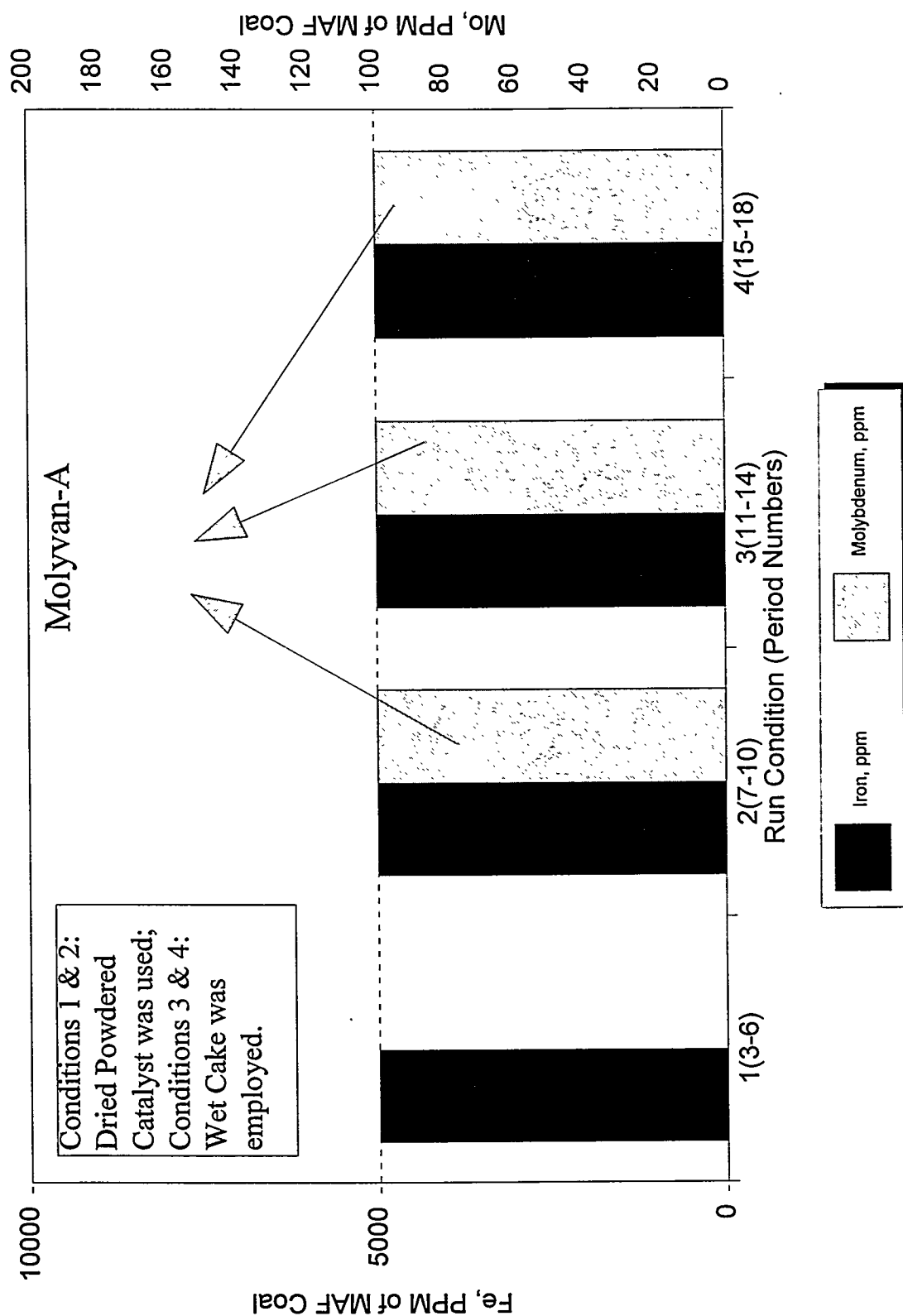


FIGURE 16

CMSL-10: Dispersed Catalysis Total Coal Conversion

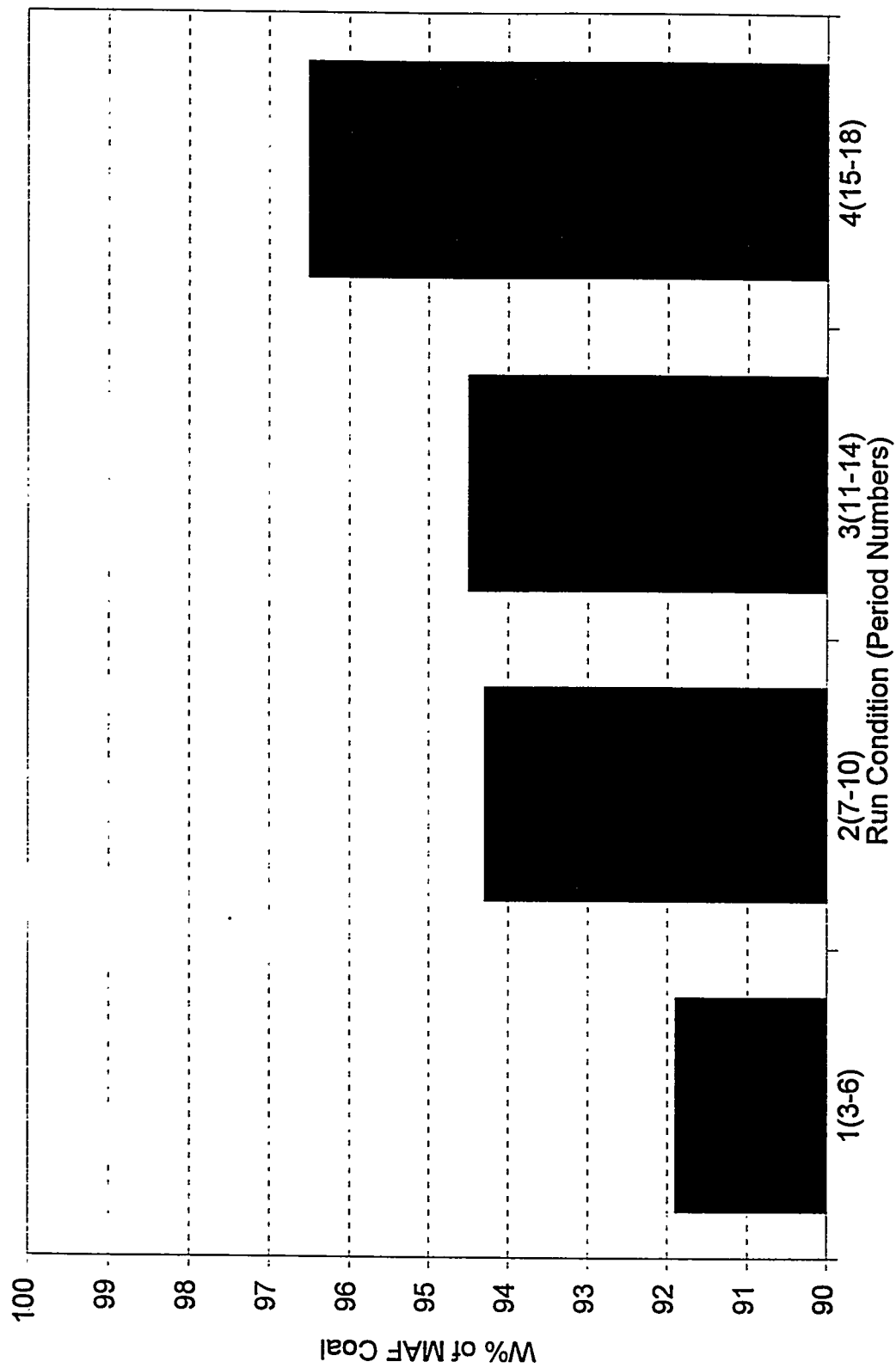


FIGURE 17

CMSL-10: Dispersed Catalysis

Total 524 C+ Resid Conversion

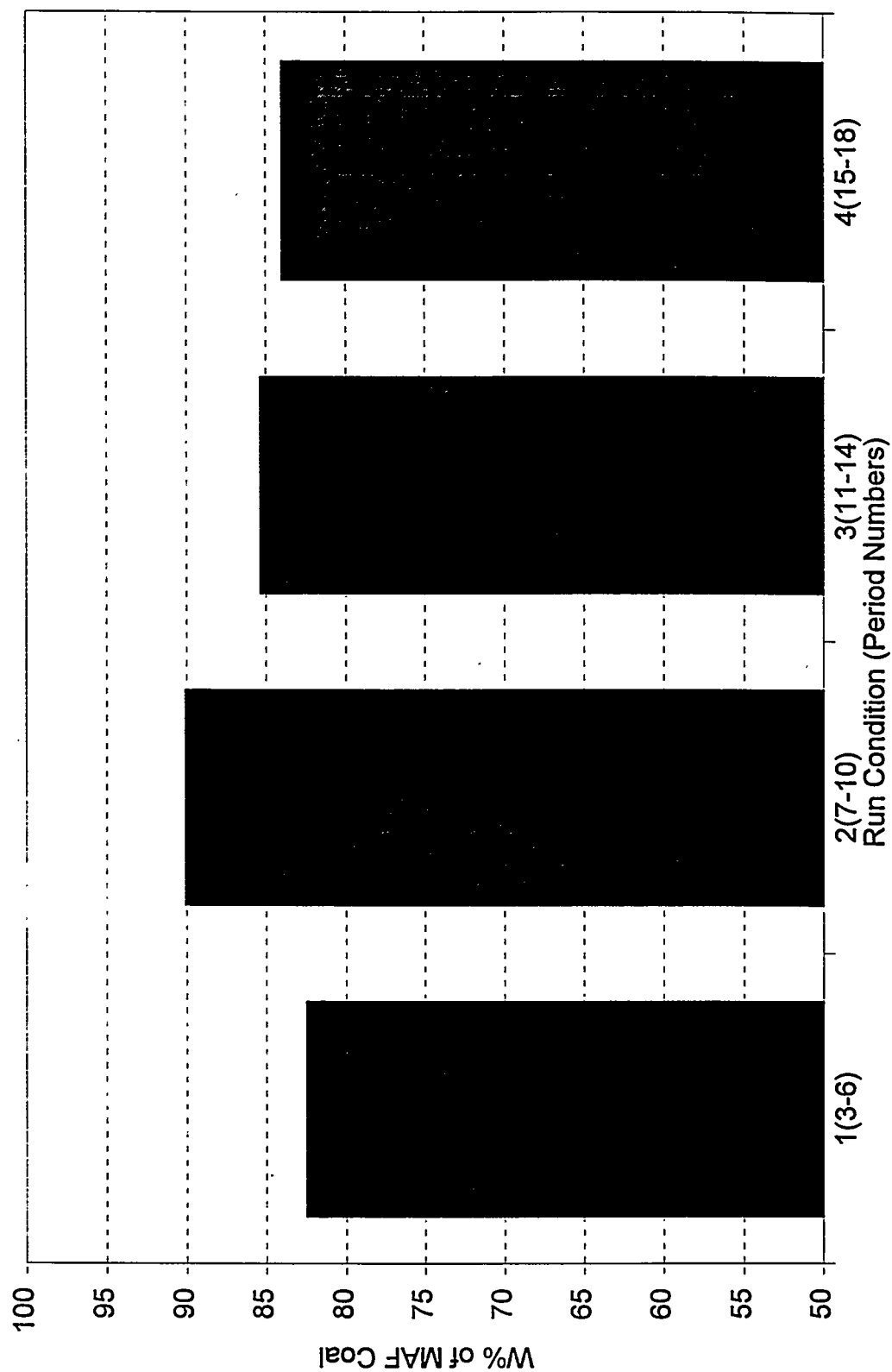


FIGURE 18

CMSL-10: Dispersed Catalysis

C4-524 C Distillate Yields

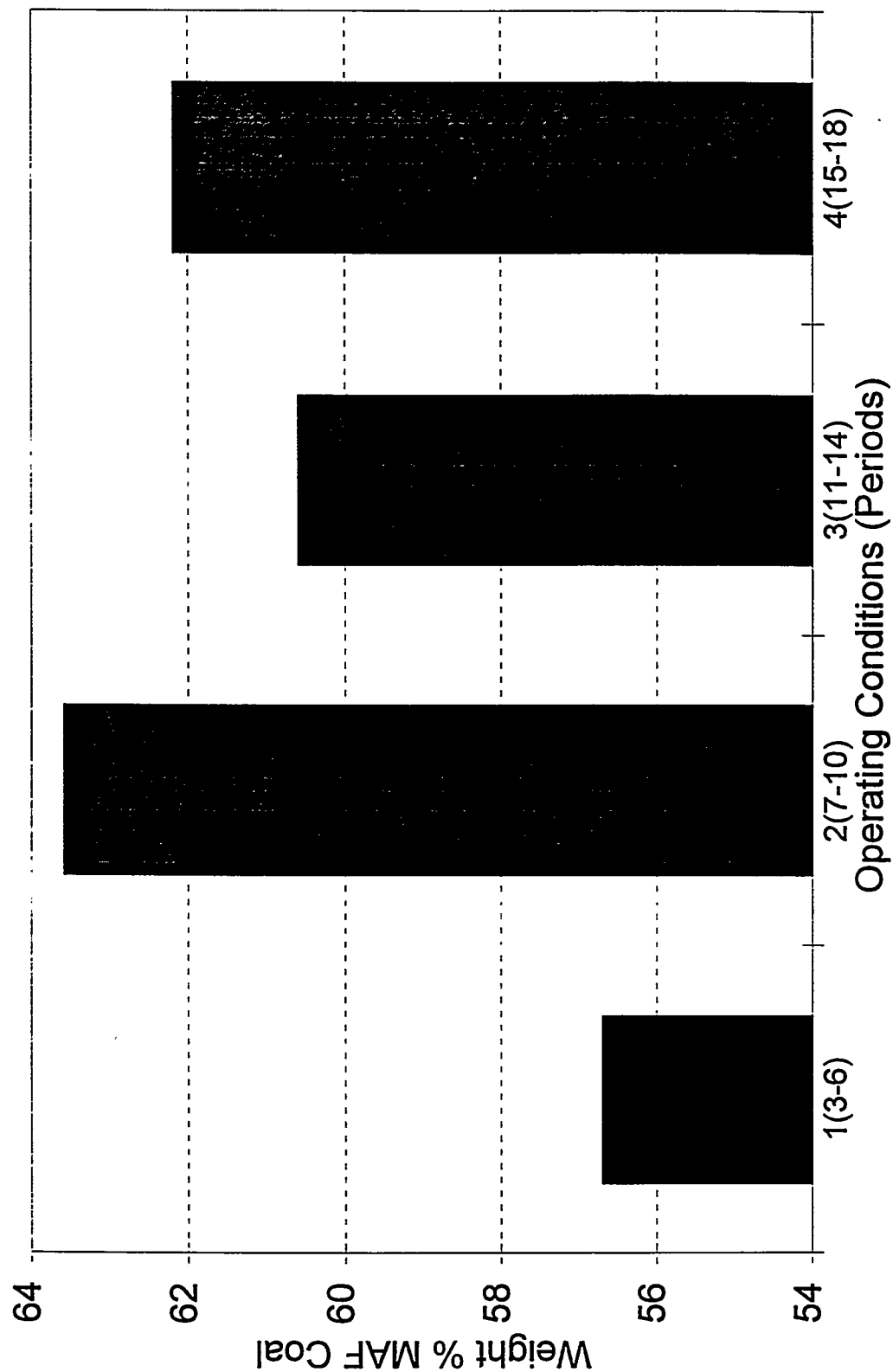


FIGURE 19

CMSL-10 : Distillate Selectivity

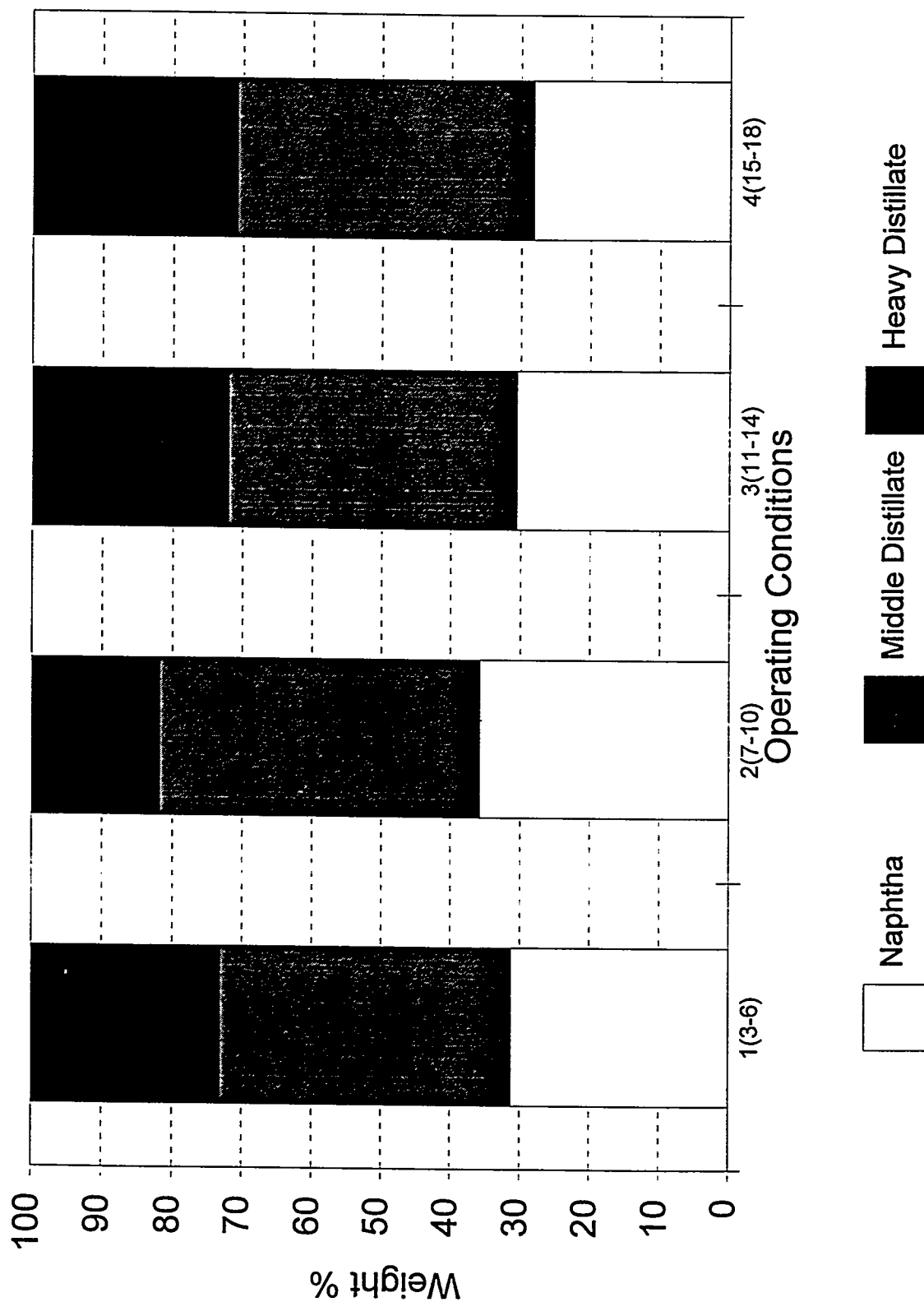


FIGURE 20

CMSL-10: Dispersed Catalysis Chemical Hydrogen Consumption

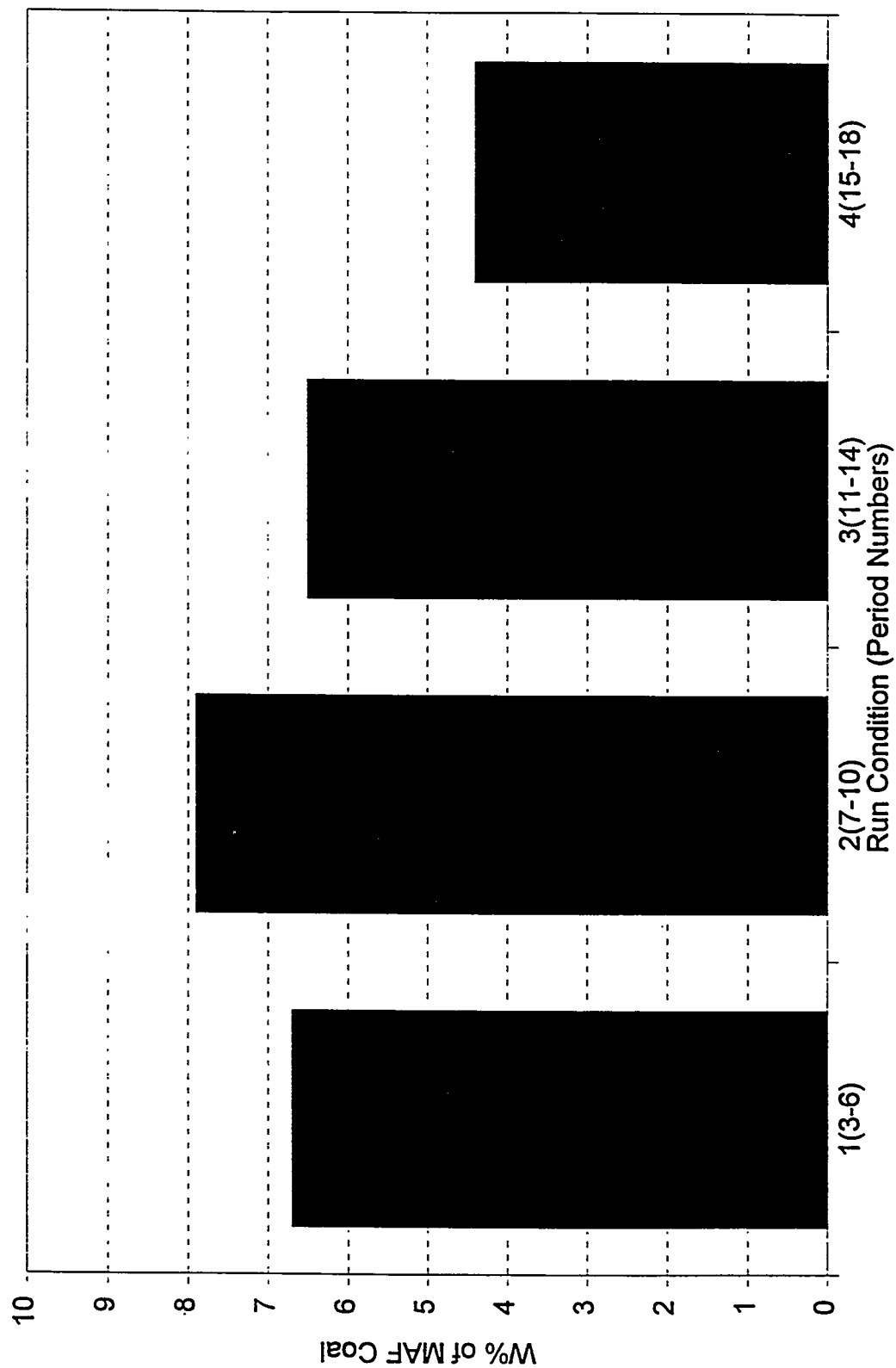


FIGURE 21

CMSL-10: Dispersed Catalysis
Light C1-C3 Gas Yield

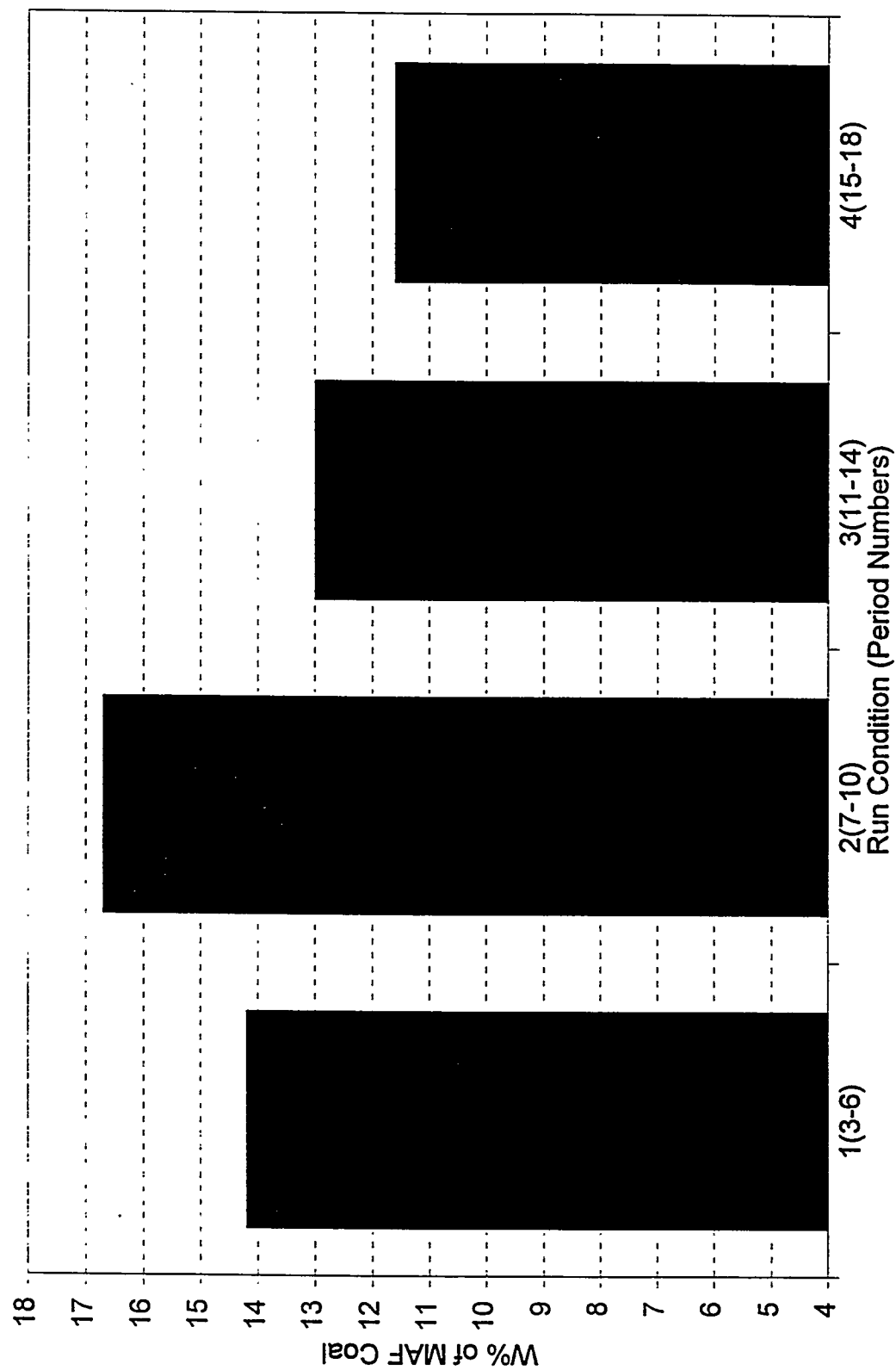
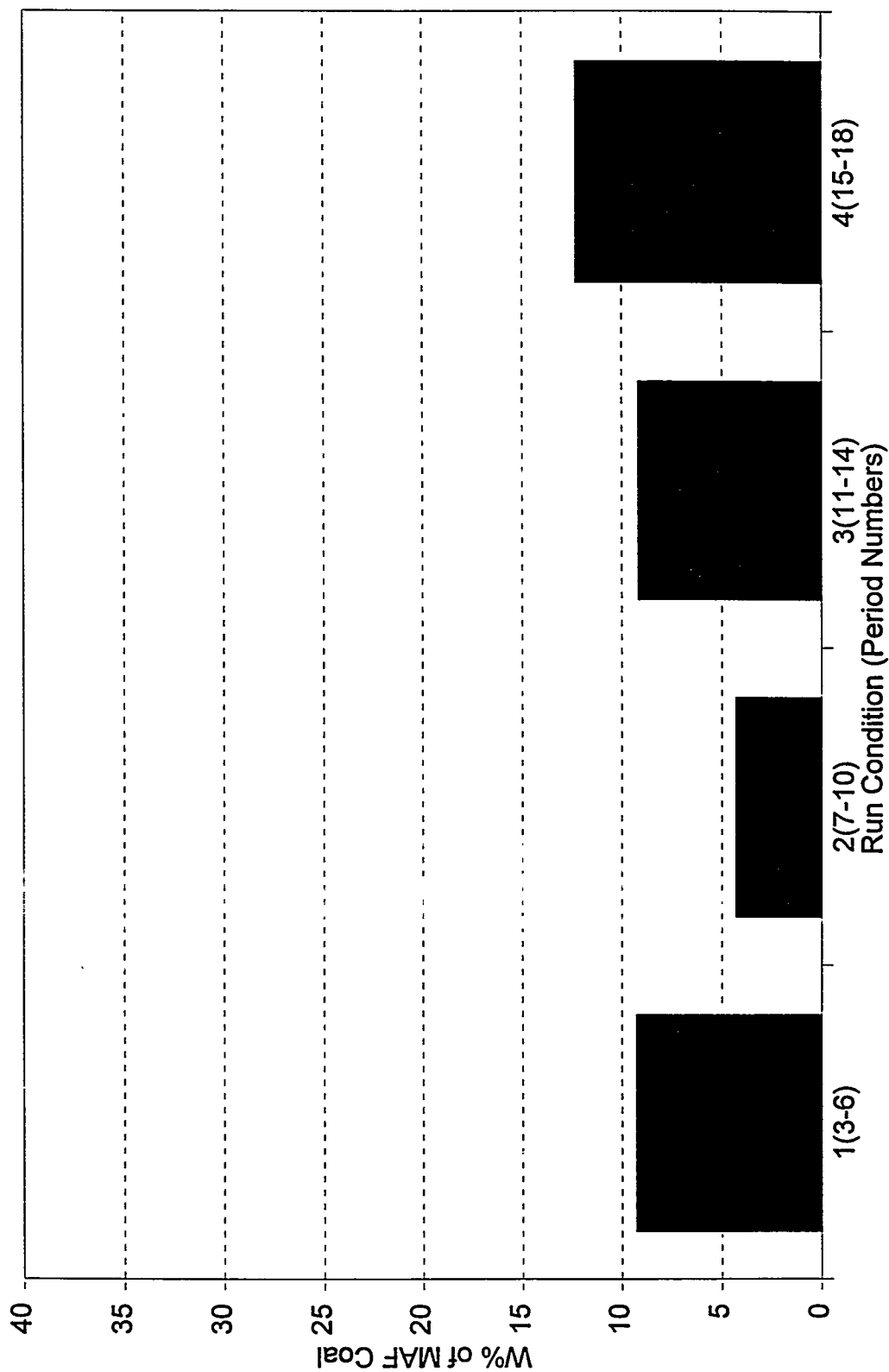


FIGURE 22

CMSL-10: Dispersed Catalysis

Total 524 C+ Resid Yield



CMSL-10: Dispersed Catalysis Solubility of PFL Product

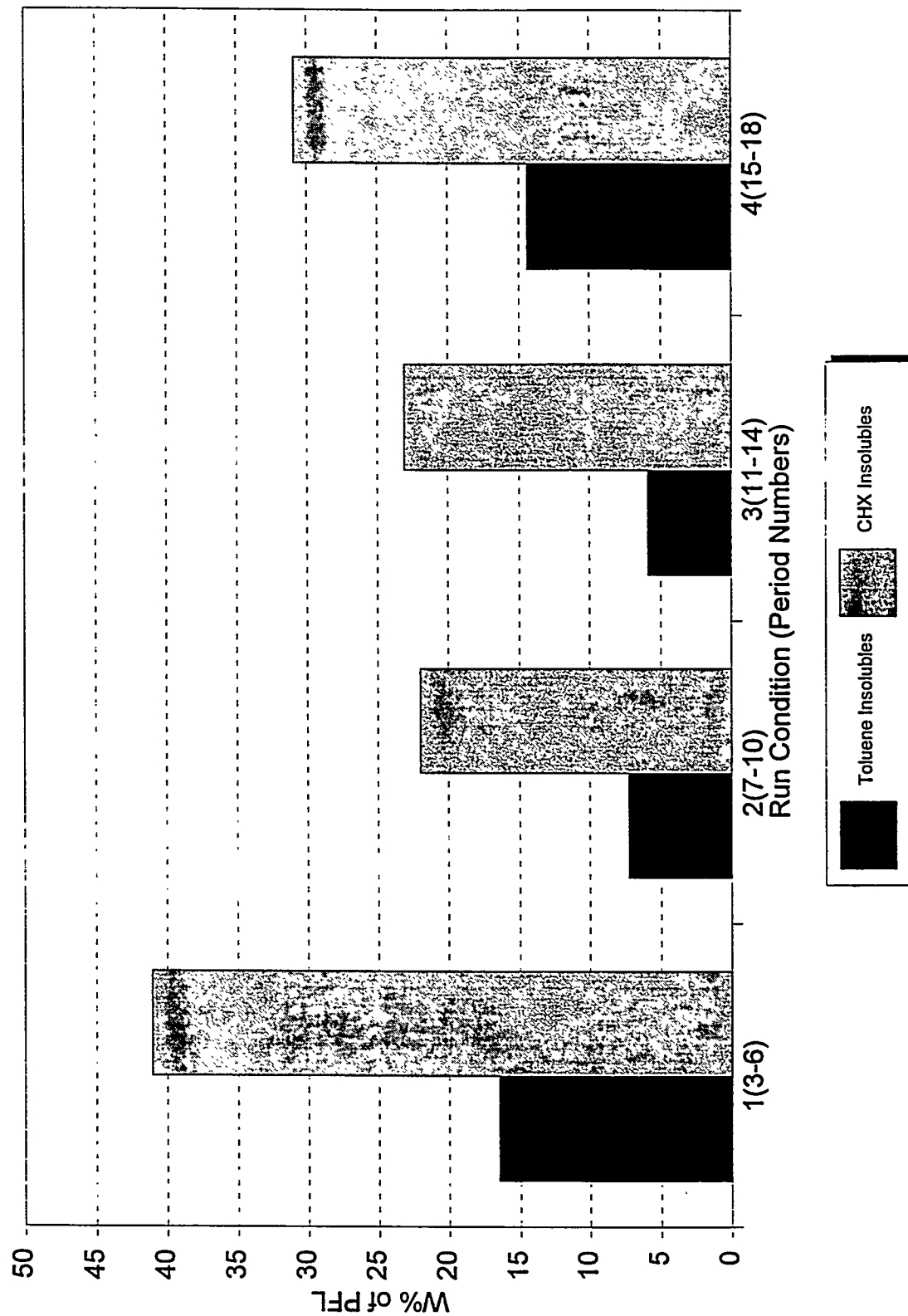
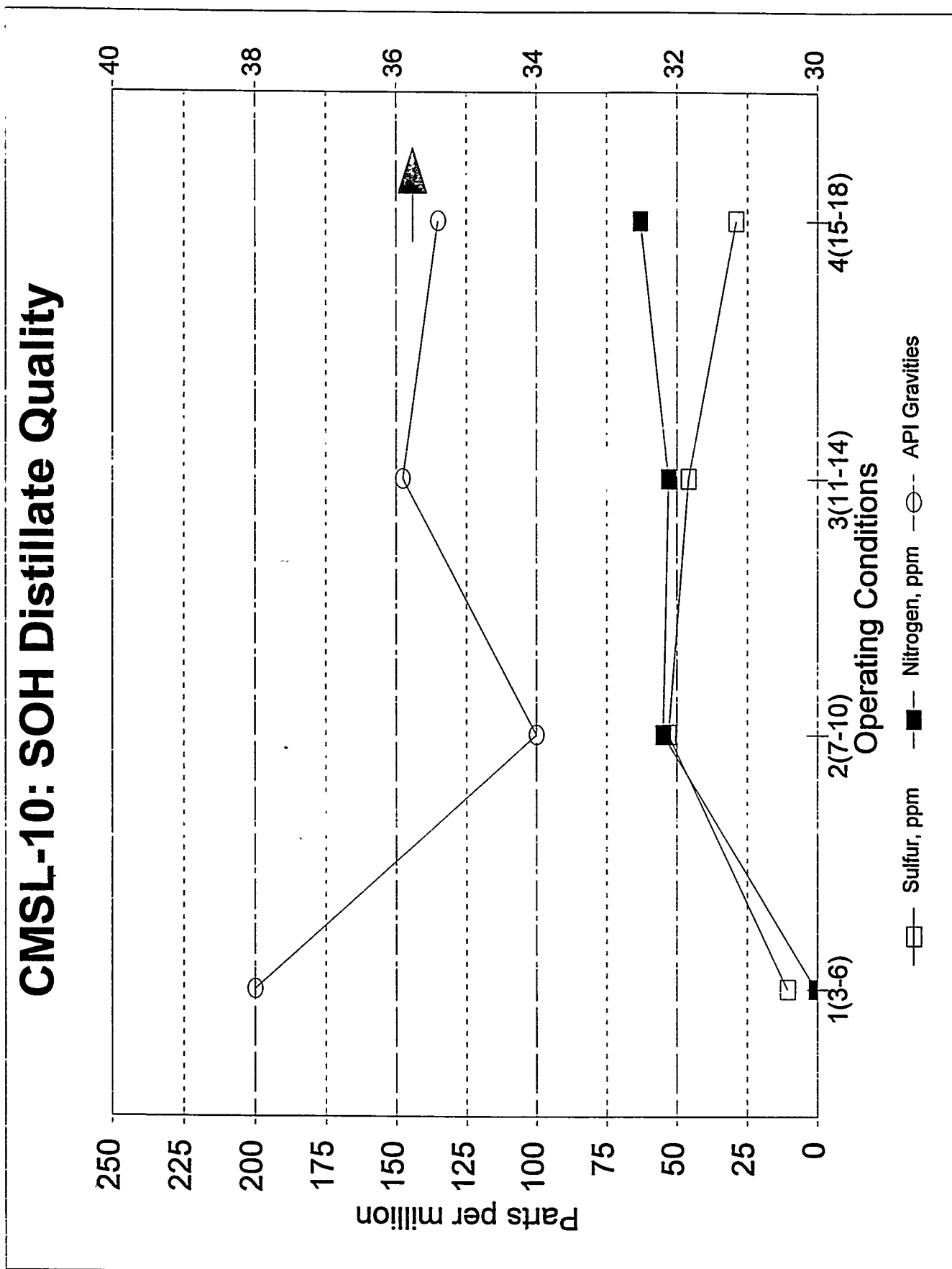


FIGURE 24



TASK 4- TECHNICAL ASSESSMENT

No technical assessment activity was conducted during this quarter.

TASK 5- PROJECT MANAGEMENT

A paper for was prepared during this quarter for the DOE Contractors' Review Meeting to be held in Pittsburgh, PA, and for the CFFLS Ninth Annual Meeting to be held in Pipestem, WV, both during August 1995.